

ИЗВЕСТИЯ
АКАДЕМИИ НАУК СССР
ОТДЕЛЕНИЕ
ХИМИЧЕСКИХ НАУК

Number 10
October, 1960

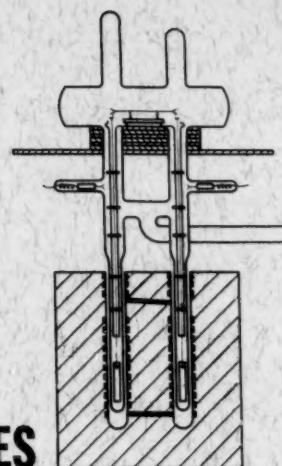
BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

Division of Chemical Science
(IZVESTIYA AKADEMII NAUK SSSR)
(Otdelenie Khimicheskikh Nauk)

IN ENGLISH TRANSLATION



CONSULTANTS BUREAU, INC.



VOLUME I VACUUM MICROBALANCE TECHNIQUES

Proceedings of the 1960 Conference Sponsored by
The Institute for Exploratory Research
U. S. Army Signal Research and Development Laboratory

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The proceedings of this conference provide an authoritative introduction to the rapidly widening scope of microbalance methods which is not available elsewhere in a single publication.

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170 pages

\$6.50



PLENUM PRESS, INC. 227 West 17th St., New York 11, N. Y.

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A publication of the Academy of Sciences of the USSR

IN ENGLISH TRANSLATION

Year and issue of first translation:

No. 1

Jan.-Feb. 1952

	<i>U. S. and Canada</i>	<i>Foreign</i>
<i>Annual subscription</i>	<i>\$80.00</i>	<i>\$85.00</i>
<i>Annual subscription for libraries of nonprofit academic institutions</i>	<i>30.00</i>	<i>35.00</i>
<i>Single issue</i>	<i>10.00</i>	<i>10.00</i>

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THE JULY PLENUM OF THE CENTRAL COMMITTEE OF THE COMMUNIST PARTY OF THE SOVIET UNION AND OUR NEW TASKS

Translated from *Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk*, No. 10, pp. 1729-1730, October, 1960

The July Plenum of the Central Committee of the Communist Party of the Soviet Union (CC of the CPSU) considered the extent of fulfillment of the resolution of the Twenty-first Party Conference on the development of industry and transport and on the application to production of the important achievements of science and technology. Leading figures and innovators in production and a number of scientists and designers took part in the work of the Plenum, in addition to Party and Soviet leaders and economists. The Plenum summed up the work on fulfillment of the Seven Year Plan for the past year and a half, and suggested concrete measures to ensure the further growth of tempo of technical progress in all branches of the national economy.

The Plenum noted that the program adopted at the Twenty-first Conference of the CPSU to provide a material and technical basis for Communism is being successfully fulfilled. The public movement for the fulfillment of the Seven Year Plan before the appointed time and the strengthening of the leadership by party organizations in economic construction have made it possible considerably to exceed the planned tempo in the growth of industrial production and the development of transport. In the Plenum decree it was noted that the program of the May (1958) Plenum of the CC of the CPSU for the more rapid development of chemical industry had been successfully realized. Taking the 1957 production as unity, the production in the current year of synthetic resins and plastics will be 1.5, that of chemical fibers 1.4, and that of synthetic alcohol almost 3. The Plenum noted the progress in all branches of the national economy is indissolubly associated with progress in Soviet sciences and with the distinguished achievements of our scientists. Academician A. N. Nesmeyanov, in his contribution to the Plenum, stated that, in the chemical field, the last two years had been marked by an enormous increase in the volume of work on polymers. A number of new compounds have been produced, including silicoorganic polymers characterized by high thermal stability, elasticity, and improved dielectric properties. The work on stereospecific polymerization has enabled our industry to produce new forms of synthetic rubber, with properties in no way inferior to natural rubber, as well as polymers for making plastics and fibers. New forms of polyacrylic esters have been produced, and these have been used in the electrical industry to improve the quality of electrical machine output; their use has led to a great reduction in the time required for impregnating and drying electrical windings. The experimental production of a new synthetic fiber, énant, has been developed by the Academy of Sciences of the USSR in cooperation with industry. A. N. Nesmeyanov stated that empiricism was a serious fault in scientific research on polymers, and he called for a strengthening of theoretical work in this important branch of chemistry.

In one of its resolutions, the Plenum condemned the slow tempo of the introduction of some progressive technological processes, and the inadequate effects of mechanization and automation on production. There was also the opposite case that newly created equipment and instruments did not always satisfy present requirements. The Plenum drew the attention of all party and economic organizations, and of all scientific workers and technologists, to the need for increasing the effectiveness of the work of all scientific research and planning institutes and design offices, and for shortening the time taken for scientific research and design work, and for introducing the results into production. The Plenum planned to improve the leadership of scientific institutions, to strengthen the coordination of their activities, to liquidate unnecessary parallelism and too narrow minded approach to a

target, to avoid the inclusion of unreal items in the plan, to consolidate the research, planning, design, and experimental basis, and to improve the dissemination of technical information. The Plenum recommended that the scientific research institutes should combine the creative work of scientists, engineer-technologists, planners, designers, and factory workers in the creation of progressive technological processes and new techniques in all stages of development from the laboratory to production, in order to strengthen their link with production, and that they should be daily concerned with the application of their achievements to industry. The Plenum proposed that the State Economic Soviet of the USSR, the State Planning Commission of the USSR, the State Scientific and Technical Committee of the Soviet of Ministers of the USSR, together with the State Committees for the different branches of industry and construction and the Soviets of Ministers for the Union Republics, should develop and draw up recommendations for improving the planning and coordination of important research, experimental, and planning work, and for the control of its application.

The Plenum of the CC of the CPSU has guaranteed that Party organizations, Councils of National Economy, and government departments will develop and put into practice measures to speed up the introduction of scientific and technical achievements into industry. It has also stated that there is a need to concentrate the attention of collective undertakings, scientific research specialists, designing and planning organizations, and higher educational establishments primarily to those problems whose solution will have the greatest economic effect and will save time. Particular attention should be directed to the production of new industrial materials, especially synthetic materials, and their wide application in different branches of industry.

The Plenum of the CC of the CPSU has called for a greater increase in creative initiative in the struggle for further acceleration of technical progress, for improving quality, and for the early fulfillment of the Seven Year Plan. The Plenum has expressed confidence that our people will do their utmost to achieve new victories and to build up communism in our land.

THE THERMAL DECOMPOSITION OF CHROMYL CHLORIDE AND THE FORMATION OF POLYCHROMYL DICHLORIDES $(CrO_2)_nCl_2$

S. Z. Makarov and A. A. Vakhrushev

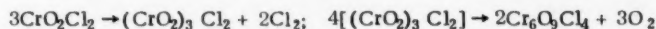
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1731-1738, October, 1960

Original article submitted June 15, 1960

There have been no systematic scientific investigations of the process of thermal decomposition of chromyl chloride, and there is very little data in the literature. The decomposition products from chromyl chloride which have been described can be divided into a few groups. Thorpe [1], Emerson [2], Pascal [3], Moles and Gomez [4], and Kantzer [5] found that the compounds $Cr_5O_{10}Cl_6$ and $Cr_3O_6Cl_2$ could be obtained by heating or chemical treatment of chromyl chloride, and that CrO_2 was the end product of the decomposition. The compound $(CrO_2)_3Cl_2$ is quite probable, but the other, $(CrO_2)_5Cl_6$, requires very serious confirmation. Herfeld [6] observed the compound $Cr_2O_5Cl_2$, which may be considered as a derivative of CrO_2Cl_2 and CrO_3 , i.e., $CrO_2Cl_2 \cdot CrO_3$.

Pascal [3] described a product $Cr_6O_9Cl_4$. The formation of such a compound must be associated with reactions liberating elementary chlorine or, possibly, its oxides. It must be presumed that, if $Cr_6O_9Cl_4$ exists, it must be formed by supplementary decomposition of $(CrO_2)_3Cl_2$ with evolution of oxygen, in accordance with the reactions



Meyer and Best [7] treated CrO_2Cl_2 with hydrogen chloride and obtained $Cr_3O_3Cl_8$, which may be considered as an interaction product of CrO_2Cl_2 and $CrCl_3$. Wöhler [8] obtained Cr_5O_9 by passing CrO_2Cl_2 vapor through a tube heated to 300°. The possibility cannot be excluded that this Cr_5O_9 was a mechanical mixture of chromium oxides, $3CrO_2 + Cr_2O_3$.

The triangular diagram (Fig. 1), constructed from the literature data with a coordinate system $Cr-Cl_2-O_2$, introduces some clarity into the results obtained by different authors, and was used as a basis for our investigation of the process of thermal decomposition of chromyl chloride. The literature data is characterized by an unusual variation in the composition of the products obtained, associated with a wide scatter of the points shown in the chemical diagram.

The reason for our investigation of the process of thermal decomposition of chromyl chloride was a need to determine the direction of the reactions occurring and the actual compositions of the products.

Experimental

It was a difficult task to investigate the process of thermal decomposition of chromyl chloride at high temperatures. The work was greatly complicated by the following factors—the high toxicity of chromyl chloride, its oxidizability and the possibility of flames, the high pressure of the vapor and its decomposition products, the need for careful control of the conditions to avoid interaction with water and dangerous explosions, etc.—so that very great care was required.

The decomposition was investigated under isothermal conditions, in an air thermostat, in the temperature range 120-255. A difference from earlier methods of investigation was that the isothermal decomposition

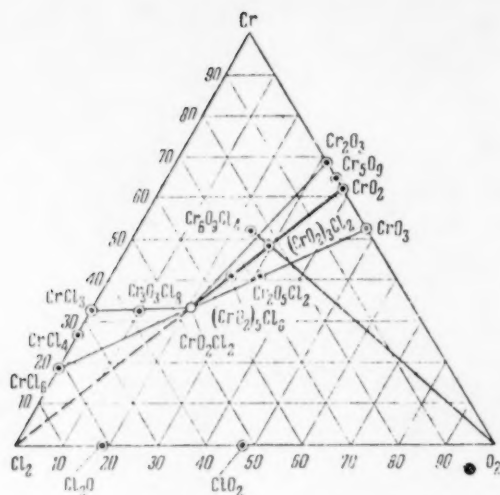


Fig. 1. Composition of the thermal decomposition products of CrO_2Cl_2 shown in a $\text{Cr}-\text{Cl}_2-\text{O}_2$ diagram, according to literature data.

The condensed products, consisting of solid materials and residual liquid chromyl chloride, were transferred to a flask with a ground stopper, using pure dry carbon tetrachloride. The ampoule was washed out into the flask with the carbon tetrachloride, in which chromyl chloride is readily soluble. The solid products were then filtered off, washed with carbon tetrachloride, and freed from solvent by heating. They were then analyzed for chlorine and for chromium by redox titration with ferrous ammonium sulfate and back titration with potassium permanganate. The oxygen was determined by the difference.

The Decomposition of Chromyl Chloride at 120, 135, 150, 180, 200 and 255°

As a Function of Temperature and Time

The extent of decomposition of chromyl chloride, as a function of temperature and time, was determined from the quantities of solid and gaseous decomposition products and of residual liquid CrO_2Cl_2 ; the latter is readily soluble in carbon tetrachloride, and was completely extracted by it. The experimental results for the temperature range 120-255° are shown in Table 1.

Isotherms for chromyl chloride decomposition at 120, 135, 150, 180, 200, and 255° were constructed from the data in Table 1 and are shown in Fig. 2. These show that the decomposition was strongly dependent on temperature and time, and increased with increasing temperature and longer time. The isotherms formed a regular system of hyperbolic curves, the curvature increasing with temperature. The 120° isotherm was practically a straight line, while at higher temperatures the extent of decomposition increased rapidly at first and then altered very little.

The Kinetics of the Evolution of Gaseous Products in the Thermal Decomposition of Chromyl Chloride and the Composition of these Products

The gases produced by the thermal decomposition of chromyl chloride were under high pressure in the ampoules; their determination required special care as there was danger of the ampoule bursting with consequent loss of gaseous products. The ampoule was first refrigerated, a light scratch was made with a file near one end, and this end was then connected to the absorption tube with polyvinyl chloride tubing and broken off inside the tubing. In this way there was no loss of gas, and the latter came out evenly rather than in a sudden burst. The ampoule was allowed to warm up gradually to room temperature, when gas evolution was practically completed. The results obtained at 120, 150, 180, 200, and 255° are tabulated in Table 2 and shown diagrammatically in Fig. 3.

was carried out in special sealed glass ampoules, and the solid and gaseous products were analyzed. In some cases, the ampoules burst when they had been kept in the thermostat for a long time at high temperatures, and sometimes there was a considerable explosion so that the glass was reduced to a fine powder. Following the advice of Mendeleev [9], we paid particular attention to the external diameter and wall thickness. Our tubes were of external diameter 11.5 to 13.0 mm and of wall thickness 1.5 to 3.0 mm. These tubes would stand the internal pressure developed up to a temperature of 255°. Sealed ampoules, containing 2-3 g of CrO_2Cl_2 , were maintained at the required temperature in the air thermostat for a definite time and then cooled. The gaseous product, which we showed to be chlorine, was passed through an absorption tube containing concentrated caustic alkali solution. The total weight of gaseous products was found from the difference in weight of the ampoule before opening and after letting out the gas. The chlorine was determined gravimetrically as AgCl after reduction to chloride ion with ferrous ammonium sulfate and dilute sulfuric acid. The gas unabsorbed by alkali (oxygen was produced above 200°) was found from the volume of water displaced from a buret.

TABLE 1

The Extent of Decomposition of Chromyl Chloride for Different Temperatures and Times

Temperature, °C	Time, hr.	Weight CrO_2Cl_2 g	Solid + gaseous decomp. products, %	Residual CrO_2Cl_2 sol. in CCl_4 , %
120	24	2,6962	2,75	97,25
	48	2,2978	6,68	93,32
	120	2,1631	18,95	81,05
	192	1,7919	30,52	69,48
	216	1,7394	32,63	67,37
	240	1,8267	37,86	62,14
	312	1,8591	49,12	50,88
135	24	1,6240	18,55	81,46
	48	1,0093	33,52	66,48
	120	1,1448	63,83	36,17
	168	1,2012	71,43	28,57
	192	1,7623	75,14	24,86
	240	1,1614	76,39	23,61
150	12	2,2748	31,55	68,45
	24	2,1109	58,90	41,10
	48	1,9690	76,61	23,39
	72	1,7698	84,32	15,68
	120	2,2303	88,73	11,27
	168	1,8148	91,58	8,42
	216	1,7262	92,88	7,12
	240	1,7422	93,28	6,72
180	0,5	2,1876	12,66	87,34
	1,0	2,1233	29,51	70,49
	3,0	2,1920	61,16	38,84
	6,0	2,1018	78,76	21,24
	12	1,9840	84,61	15,39
	24	1,9053	87,80	12,20
	48	1,9210	90,00	10,00
	96	2,1987	92,92	7,03
	192	2,2283	95,47	4,53
	240	2,1368	96,28	3,82
200	2,0	2,2988	88,25	11,75
	12	2,4716	93,15	6,85
	48	2,3423	94,20	5,80
	96	2,3237	96,73	3,27
	192	2,7041	99,23	0,77
	240	2,3767	99,80	0,20
255	1,0	1,2871	74,09	25,91
	6,0	1,3422	93,28	6,72
	12	1,3148	96,00	4,00
	48	1,9657	97,28	2,72
	72	2,4696	99,02	0,98

The curves of Fig. 3 are characterized by a marked increase with temperature and a marked attenuation with time. It is clear that time was required to stabilize the gas formation. Equilibrium was reached when the amount of gas formed became constant. The effect of temperature on the time required to reach equilibrium can be seen from Fig. 3.

Analysis of the gas showed that there was no significant amount of oxygen up to 200°, but that oxygen evolution was appreciable at 255°. Only chlorine was produced over a wide temperature range. It followed that the thermal decomposition of CrO_2Cl_2 could be represented by the equation:

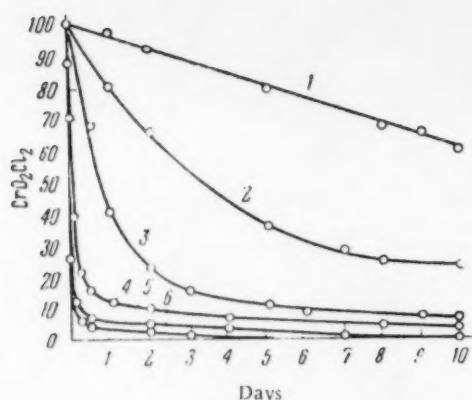


Fig. 2. The change in CrO_2Cl_2 content, as the result of thermal decomposition, as a function of time, at temperatures 1) 120° , 2) 135° , 3) 150° , 4) 180° , 5) 200° , 6) 255° .

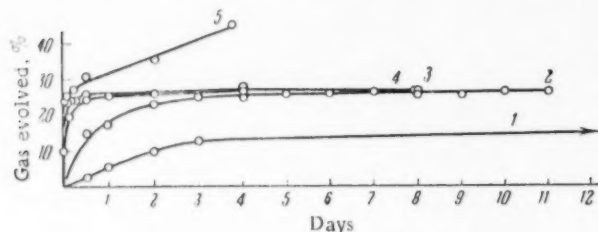


Fig. 3. Kinetic curves for the evolution of gaseous products in the thermal decomposition of CrO_2Cl_2 at 1) 120° , 2) 150° , 3) 180° , 4) 200° , 5) 255° .

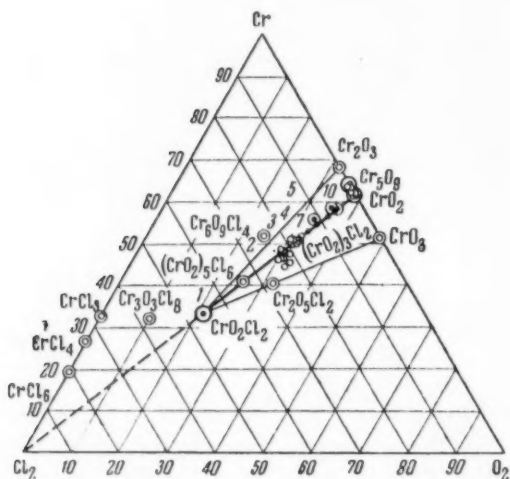
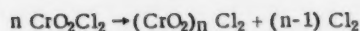


Fig. 4. The experimental data for the compositions of solid thermal decomposition products of CrO_2Cl_2 , shown on a $\text{Cr}-\text{Cl}_2-\text{O}_2$ diagram.



The Chemical Composition of the Solid Phase Obtained in the Thermal Decomposition of Chromyl Chloride

The investigation of the solid phase obtained by the thermal decomposition of chromyl chloride was of the greatest interest. The solid products obtained were analyzed for chromium and chlorine, and the oxygen was determined by difference. The results obtained are tabulated in Table 3 and shown diagrammatically in Fig. 4.

These results showed that the elementary composition of the material depended on the time and temperature of heating. It is highly significant that the points corresponding to the compositions found for the solid products were distributed about the straight line $\text{Cl}_2-\text{CrO}_2\text{Cl}_2-\text{CrO}_2$. This confirmed what is suggested above that the basic reaction of CrO_2Cl_2 decomposition was the formation of polychromyl chlorides. Most of the experimental points on the diagram were grouped about the point corresponding to the composition $(\text{CrO}_2)_3\text{Cl}_2$. This confirmed that the main decomposition process was the reaction $3\text{CrO}_2\text{Cl}_2 \rightarrow (\text{CrO}_2)_3 + 2\text{Cl}_2$, producing the so-called tri-chromyl chloride. There were no points corresponding to phases with $n < 3$, such as $(\text{CrO}_2)_2\text{Cl}_2$, which might be formed as intermediate products. This was because polychromyl chlorides containing less than three CrO_2 groups per molecule are semiliquid and soluble in CCl_4 , in the same way as chromyl chloride which can be considered as monochromyl chloride. There was also a considerable accumulation of experimental points on the diagram in the region of the compound $(\text{CrO}_2)_4\text{Cl}_2$.

When trichromyl chloride was heated in the open, chlorine split off and tetrachromyl chloride was formed in accordance with the reaction: $4(\text{CrO}_2)_3\text{Cl}_2 \rightarrow 3(\text{CrO}_2)_4\text{Cl}_2 + \text{Cl}_2$.

Further decomposition occurred when the solid product from heating CrO_2Cl_2 at 200° for 1.5 days was further heated to 255° for 1.5 hr (Table 4).

This showed that $(\text{CrO}_2)_4\text{Cl}_2$ was converted into $(\text{CrO}_2)_7\text{Cl}_2$. When CrO_2Cl_2 was heated to 255° for 2 days, the process was completed by the formation of CrO_2 containing no chlorine. Experiment showed that, when this CrO_2 was further heated, it gave up oxygen to form Cr_5O_3 , a change in the direction of conversion to Cr_2O_3 . This in-

intermediate oxide can be considered as $3\text{CrO}_2 \cdot \text{Cr}_2\text{O}_3$. Intermediate products between $(\text{CrO}_2)_4\text{Cl}_2$ and CrO_2 were obtained by additional thermal treatment of the solid phases (Table 5).

TABLE 2

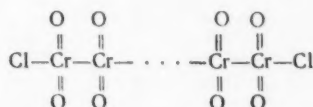
Relative Quantities of Gaseous Decomposition Products of Chromyl Chloride

Temperature, °C	Time, hr.	Weight CrO_2Cl_2 , g	Gaseous products, %	Temperature, °C	Time, hr.	Weight CrO_2Cl_2 , g	Gaseous products, %
120	12	2,2446	2,60	180	48	1,9210	25,85
	24	2,6962	5,50		72	2,1937	27,06
	48	3,2978	10,05		192	2,2283	27,25
	72	3,0016	12,71	200	0,5	2,5402	10,08
	312	1,8591	14,80		2,0	2,2983	23,73
150	456	2,8247	15,47		2,0	1,7395	23,34
	12	2,4809	14,91		4,0	2,3277	24,00
	24	1,9600	17,14		6,0	2,4662	24,10
	48	2,5493	22,77		12	2,4716	26,52
	72	2,3786	25,80		12	2,3767	26,41
	96	4,3292	25,39		24	2,6727	26,72
	120	3,0456	26,77		24	2,4494	26,21
	144	2,0560	26,80		48	2,3423	26,12
	168	2,4408	27,23		96	2,4178	28,11
	192	1,3634	26,64		192	2,7341	27,00
	216	2,3499	26,54	255	1,0	1,2340	23,72
	240	2,2909	27,40		2,0	1,4938	24,83
	264	3,4450	27,23		6,0	1,4284	27,23
180	0,5	2,1876	0,50		12,0	1,3896	30,00
	3,0	1,7463	19,47		48	1,3883	35,45
	12,0	1,9340	24,81		90	2,4636	46,20
	24	1,9053	25,48				

These solid products slowly absorbed moisture from the atmosphere and decomposed giving off chlorine (as well as CrO_2); they were thus converted into dark brown liquids. They were quite stable in the absence of moisture, and readily dissolved in water giving off chlorine. They dissolved in alkali to give yellow salts of chromic acid and amorphous green hydrated chromium oxide.

Summary

1. The process of thermal decomposition of chromyl chloride has been investigated over the temperature range 120–255°, and the solid, liquid, and gaseous products have been analyzed completely.
2. The analysis of the products shows that chlorine is evolved up to 200°, and oxygen at higher temperatures. The results have been plotted on a triangular $\text{Cr}-\text{Cl}_2-\text{O}_2$ diagram and lie on a straight line joining Cl_2 to CrO_2 , i.e., on the line $\text{Cl}^2-\text{CrO}_2\text{Cl}_2-\text{CrO}_2$.
3. The products found, namely $(\text{CrO}_2)_3\text{Cl}_2$, $(\text{CrO}_2)_4\text{Cl}_2$, etc., as well as CrO_2Cl_2 , belong to the class of poly-chromyl chlorides $(\text{CrO}_2)_n\text{Cl}_2$, of general structure



4. The further thermal decomposition of CrO_2 is associated with loss of oxygen and formation of the intermediate product Cr_5O_9 , and finally of Cr_2O_3 .

TABLE 3

The Compositions of the Solid Decomposition Products of Chromyl Chloride

Experi- ment temp. °C.	Time, hr.	Composition, %			Extraction conditions		Solid Residue Formula			
		Cr	O ₂	Cl ₂	Temp., °C	Time, hr.	Mole ratio			Probable solid phase
							Cr	O	Cl	
120	192	46,02	32,00	21,98	80	0,5	2,8	4,5	2,0	(CrO ₂) ₃ Cl ₂ The same
	312	47,72	29,36	22,92	80	0,5	2,8	5,6	2,0	
	360	47,96	29,68	22,36	80	0,5	2,9	5,9	2,0	
135	24	49,47	29,05	22,48	135	0,5	2,9	6,0	2,0	(CrO ₂) ₃ Cl ₂
	96	48,05	29,66	22,26	135	3	2,9	5,9	2,0	The same
	168	50,94	32,00	17,06	200	1	4,0	8,3	2,0	(CrO ₂) ₄ Cl ₂
	216	51,08	31,46	17,46	135	12	4,0	8,0	2,0	The same
150	24	47,01	30,21	22,78	80	0,5	2,8	6,6	2,0	(CrO ₂) ₃ Cl ₂
	168	46,57	29,81	23,62	80	0,5	2,8	5,6	2,0	The same
	192	48,85	29,15	22,00	150	2	3,0	6,0	2,0	(CrO ₂) ₄ Cl ₂
	264	50,36	32,16	17,46	150	2	3,9	8,0	2,0	
180	3	46,71	30,6	22,60	80	1	2,8	6,6	2,0	(CrO ₂) ₃ Cl ₂
	12	48,41	29,41	22,07	80	1	3,0	6,6	2,0	(CrO ₂) ₃ Cl ₂
	24	47,51	30,69	21,71	80	1	3,1	6,0	2,0	The same
	96	48,06	30,35	21,62	80	1	3,1	6,0	2,0	»
	192	48,73	28,82	22,45	80	1	3,1	6,0	2,0	»
200	4	47,86	30,17	21,95	80	1	3,1	6,0	2,0	(CrO ₂) ₃ Cl ₂
	48	49,40	30,60	20,00	80	1	3,4	6,8	2,0	(CrO ₂) ₃ Cl ₂ + (CrO ₂) ₄ Cl ₂
	48	50,30	30,60	19,10	130	1	3,6	7,1	2,0	The same
	36	51,93	31,55	16,47	130	5	4,3	8,6	2,0	(CrO ₂) ₄ Cl ₂
	48	51,61	31,67	16,72	130	7	4,2	8,4	2,0	The same
255	1	48,07	31,11	20,82	100	1	3,1	6,6	2,0	(CrO ₂) ₃ Cl ₂ + (CrO ₂) ₄ Cl ₂
	3	51,32	30,48	18,20	80	1	3,8	7,4	2,0	The same
	5	49,92	31,55	18,53	160	1	3,7	7,5	2,0	»
	6	50,22	30,45	19,33	80	1	3,7	7,2	2,0	»
	12	51,94	31,94	16,12	80	1	4,0	8,0	2,0	(CrO ₂) ₄ Cl ₂
	48	62,48	37,52	Trace	255	0,5	1,0	1,95	—	CrO ₃
	48	60,51	39,49	None	255	0,5	1,0	2,13	—	The same
	48	62,33	37,67	»	255	0,5	1,0	1,96	—	»
	48	62,00	37,25	»	255	1	1,0	1,96	—	»
	48	63,75	35,50	»	255	2	1,0	1,81	—	Cr ₂ O ₃
	72	64,01	35,99	»	160	1	1,0	1,83	—	The same
	72	64,18	35,82	»	160	1	1,0	1,82	—	»

TABLE 4

The Change in Composition of the Polychromyl Chloride Containing 4.3 Mole of CrO₂ After Thermal Treatment

	Elementary composition, %			Total composition
	Cr	O ₂	Cl ₂	
Initial composition at 200°	51,98	31,55	16,47	(CrO ₂) _{4,3} Cl ₂
Composition after treatment at 255°	55,89	33,00	11,11	(CrO ₂) _{6,8} Cl ₂

TABLE 5

Compositions of the Solid Products Produced by Thermal Decomposition of Chromyl Chloride After Additional Thermal Treatment

Experiment number	Additional heating time	Elementary composition, %			Total composition of solid phase
		Cr	O ₂	Cl ₂	
	Initially experiment 4 at 255° in Table 3	50,22	30,45	19,33	(Cr ₂ O) _{3,5} Cl ₂
1	3 hr	57,60	33,37	9,03	(CrO ₂) _{8,7} Cl ₂
2	6 hr	57,60	35,13	7,27	(CrO ₂) _{10,8} Cl ₂

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INVESTIGATION OF THE ADSORPTION OF VAPORS ON ADSORBENTS WITH A HETEROGENEOUS SURFACE

PART 3. ANALYSIS OF THE EXPERIMENTAL DATA FOR SILICA GEL WITH A CHEMICALLY MODIFIED SURFACE

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1739-1750,
October, 1960

Original article submitted June 2, 1959

Chemical modification of a silica gel surface by substitution of surface hydroxyl groups by different radicals can, in many cases, lead to a substantial change in the adsorptive properties for inorganic and organic vapors.* There is usually a reduction in the adsorption with increasing degree of substitution. Both for the initial silica gel and for samples with a chemically modified surface, it is sufficiently accurate to use the Brunauer, Emmett, and Teller [3] equation for the adsorption isotherm:

$$a = \frac{a_m c h}{(1-h)[1+(c-1)h]}, \quad (1)$$

where h is the relative pressure. An observed reduction in adsorptive capacity is often considered as being due to a decrease in the value of the adsorption a_m calculated from Eq. (1), corresponding to the formation of a continuous monomolecular layer in terms of the BET theory.

An observed reduction in the constant a_m can be interpreted from different points of view: 1) it may be due to an actual decrease in the specific surface of the silica gel as the result of chemical modification; 2) there may be an increased molecular cross section of the adsorbate for the continuous monomolecular layer formed on the chemically changed surface of the gel; 3) the BET equation may be used in a purely formal sense, so that a_m has no real value, but only an effective value. The choice of a rational interpretation of experimental results is associated with a consideration of the fundamental reasons for a slight or significant change in the adsorptive capacity of the gel in terms of the change in chemical nature of its surface. It is, therefore, convenient to concentrate first on consideration of the results in terms of the BET adsorption isotherms and the experimental facts.

1. Table 1 shows the combined results, expressed in terms of the BET adsorption equation (1), for the silica gel samples investigated, SC and SF are the original samples of coarse and fine pore silica gels; SC-1, SC-2, SF-1, SF-2 are the same gels with their hydroxyl groups partially replaced by fluorine atoms, the extent of replacement being greater for 2 than for 1 [1]. S-1 is a silica gel with part of its hydroxyl groups replaced by CH_3 radicals; S-2 is a demethylated sample of S-1, with the CH_3 radicals replaced by OH groups [2]. Table 1 shows the values of the constants a_m and c in the adsorption isotherm Eq. (1), and the range of relative pressure, h , over which the equation fits the experimental results satisfactorily. The equilibrium relative pressure, h_m , corresponds to a value of the adsorption $a = a_m$ in equation (1), i.e., to the formation of a continuous monomolecular layer; it is calculated from equation (2), derived by substituting $a = a_m$ in Eq. (1).

*The appropriate literature references are given in the previous papers of this series [1, 2].

TABLE 1

Application of the BET Adsorption Isotherm to the Silica Gel Samples Investigated

Vapor		SC	SC-1	SC-2	SF	SF-1	SF-2	S-2	S-1
N ₂ -195°	$a_m \frac{mM}{g}$	3,35	2,86	2,42	6,53	6,49	5,62	2,16	2,03
	c	119	102	91,6	69,2	67,0	65,8	166	62,6
	Range of h	0,02-0,38	0,02-0,25	0,03-0,34	0,07-0,40	0,02-0,35	0,04-0,35	0,035-0,40	0,05-0,33
	$a_{mh} \frac{mM}{g}$	0,084	0,091	0,095	0,107	0,109	0,110	0,072	0,112
Ar -195°	$a_m \frac{mM}{g}$	3,03	2,52	2,03	7,24	6,78	5,99	—	—
	c	27,0	26,4	26,7	15,3	17,7	14,5	—	—
	Range of h	0,04-0,35	0,04-0,35	0,05-0,35	0,07-0,42	0,05-0,32	0,03-0,35	—	—
	$a_{mh} \frac{mM}{g}$	0,162	0,163	0,162	0,203	0,192	0,208	—	—
C ₆ H ₁₂ 20°	$a_m \frac{mM}{g}$	3,03	2,47	2,05	7,10	6,75	5,93	—	—
	c	0,400	0,175	0,083	0,922	0,895	0,701	0,279	0,144
	Range of h	2,62	2,40	2,83	7,75	6,69	4,95	4,25	4,26
	$a_{mh} \frac{mM}{g}$	0,05-0,25 0,332	0,10-0,35 0,393	0,10-0,35 0,372	0,02-0,11 0,263	0,02-0,14 0,275	0,04-0,18 0,312	0,08-0,27 0,326	0,11-0,30 0,326
	$a_{am} \frac{mM}{g}$	0,415	0,170	0,090	2,05	1,34	0,83	0,313	0,147

TABLE 1 (continued)

Vapor	SC	SC-1	SC-2	SF	SF-1	SF-2	S-2	S-1
C_3H_8								
$a_m \frac{mM}{g}$	1,03	0,343	0,134	2,9	1,97	1,35	0,632	0,295
c	11,4	13,7	12,9	10,2	10,7	9,90	11,1	7,72
Range of h_{hm}	0,04-0,30	0,06-0,35	0,05-0,30	0,08-0,20	0,07-0,20	0,05-0,22	0,07-0,35	0,10-0,40
$a_{hm} \frac{mM}{g}$	0,229	0,213	0,208	0,238	0,235	0,240	0,230	0,264
	1,06	0,36	0,14	3,20	2,20	1,41	0,67	0,28
H_2O								
$a_m \frac{mM}{g}$	1,74	0,642	0,421	4,47	2,34	1,70	1,01	0,482
c	11,3	55,8	39,7	11,8	15,8	16,8	22,0	33,3
Range of h_{hm}	0,05-0,32	0,05-0,32	0,05-0,30	0,05-0,35	0,05-0,33	0,07-0,35	0,03-0,40	0,04-0,32
$a_{hm} \frac{mM}{g}$	0,229	0,118	0,137	0,226	0,201	0,197	0,176	0,143
	1,60	0,80	0,50	4,30	2,40	1,78	0,98	0,50

$$h_m = \frac{\sqrt{c}-1}{c-1}. \quad (2)$$

The adsorption values a_{h_m} , also shown in Table 1, correspond to the mean value h_m for the silica gel samples of each series, derived from the adsorption isotherm graphs.

The data in Table 1 shows that for most of the adsorbent-adsorbate systems the BET adsorption isotherm equation is applicable over a normal range of h about the equilibrium relative pressure; this range is from $h = 0.05$ to 0.35 , and does not vary significantly. In the case of cyclohexane as adsorbate the range is restricted, sometimes on the low side and sometimes on the high side. Similar behavior is shown by the absorption of benzene vapor on the finely porous gels of the SF series. The equilibrium relative pressures, h_m , corresponding to a filled monolayer, are within the range of applicability of the BET equation, except for experiments with cyclohexane vapor on any of the adsorbents investigated and with benzene vapor on gels of the SF series.

The observed effect of replacing surface hydroxyl groups of the silica gel by fluorine atoms or CH_3 radicals is to decrease the constant a_m of the adsorption isotherm Eq. (1), which, according to the BET theory, represents the value of the adsorption for a continuous monomolecular layer. This change is relatively less pronounced for nitrogen and argon vapors, and more pronounced for cyclohexane, benzene, and water. In most cases, chemical modification of the surface has little effect on the value of c in the equation. However, there is rather more change in c for the S series with nitrogen and for the SC and S series with water vapor. When there is little change in c for any of the gels, h_m differs little from one adsorbate to another, and the value of a_{h_m} , interpolated from the isotherm curve for the mean value of the relative pressure h_m , is close to the capacity, a_m , of the monomolecular layer. It is only natural that, for the above mentioned case of cyclohexane vapor, a substantial difference is observed between the values of a_{h_m} and a_m .

The change in the adsorptive capacity of a silica gel, as the result of chemical modification of the surface, can be directly estimated from the relative decrease in the value of the adsorption over a characteristic range of relative pressure, such as that corresponding to normal applicability of the BET equation. For this purpose it is best to determine the affinity coefficients, γ , of the isotherms graphically and their variations from the mean values. The value of the adsorption for the original gel sample of each series is taken as unity, and the mean relative change in adsorption for the modified gel is determined over the range of relative pressure under consideration; this change is the affinity coefficient, γ , of the isotherm. Table 2 shows the relative pressure range used for determining the affinity coefficients; outside these pressure limits the adsorption isotherms cannot be compared, even with gross approximation. The relative pressure ranges shown in Table 2 correspond, in general, with the applicability ranges of the BET adsorption isotherm equation for the corresponding adsorbent-adsorbate systems.

TABLE 2

Equilibrium Relative Pressure Ranges Used for Determining the Affinity Coefficients of the Adsorption Isotherms

Vapor	Series of silica gel samples	Range of h
N_2, Ar	SC, SF, S	0,05—0,35
C_6H_{12}	SC	0,10—0,35
C_6H_{12}	SF	0,02—0,25
C_6H_{12}	S	0,04—0,32
C_6H_6	SC, S	0,05—0,35
C_6H_6	SF	0,01—0,25
H_2O	SC, SF, S	0,06—0,32

According to Table 3, the relative variations of the affinity coefficients from their mean values do not exceed 10-12%. These coefficients can therefore be used directly as approximate indices, derived from the experimental data, to characterize the relative changes in adsorptive capacity for the silica gel samples of each series.

In Table 3 there are comparisons of the relative values of the constants a_m in the adsorption isotherm Eq. (1), of the values of the absorptions a_{h_m} for the mean equilibrium pressures h_m corresponding to formation of a continuous monomolecular layer, and of the affinity coefficients, γ , of the absorption isotherms together with their variations from their mean values. The first line shows the specific surfaces of the gel samples, calculated from the constants a_m from isotherms for the low temperature adsorption of nitrogen, on the assumption that, for all the samples, the molecular cross sectional area of nitrogen in the filled monomolecular layer is the same and equal to 16.2 \AA^2 .

TABLE 3
Relative Changes in the Absorptive Capacities of Silica Gels as the Result of Chemical Modification of the Surface.

	SC	SC-1	SC-2	SF	SF-1	SF-2	S-2	S-1
Vapor	$\frac{\text{m}^3}{\text{s g}}$	326	278	236	642	632	548	204
N ₂	a m	1,00	0,85	0,72	1,00	0,93	0,85	0,96
	a hm	1,00	0,78	0,67	1,00	0,97	0,85	0,87
	γ	1,00	0,79 \pm 0,02	0,69 \pm 0,05	1,00	0,97 \pm 0,01	0,85 \pm 0,02	0,91 \pm 0,03
Ar	a m	1,00	0,82	0,68	1,00	0,94	0,83	—
	a hm	1,00	0,82	0,68	1,00	0,95	0,84	—
	γ	1,00	0,83 \pm 0,02	0,69 \pm 0,02	1,00	0,95 \pm 0,01	0,83 \pm 0,02	—
C ₆ H ₁₂	a m	1,00	0,44	0,21	1,00	0,97	0,76	0,52
	a nm	1,00	0,41	0,22	1,00	0,66	0,40	0,47
	γ	1,00	0,39 \pm 0,04	0,21 \pm 0,01	1,00	0,73 \pm 0,09	0,47 \pm 0,07	0,52 \pm 0,06
C ₆ H ₆	a m	1,00	0,33	0,13	1,00	0,67	0,46	0,47
	a hm	1,00	0,34	0,13	1,00	0,69	0,44	0,42
	γ	1,00	0,36 \pm 0,04	0,13 \pm 0,02	1,00	0,67 \pm 0,02	0,44 \pm 0,02	0,41 \pm 0,04
H ₂ O	a m	1,00	0,37	0,24	1,00	0,52	0,38	0,48
	a hm	1,00	0,50	0,31	1,00	0,56	0,41	0,51
	γ	1,00	0,50 \pm 0,10	0,32 \pm 0,08	1,00	0,57 \pm 0,02	0,43 \pm 0,03	0,52 \pm 0,03

The most complete correspondence between the three methods of expressing the relative change in adsorption capacity is observed with all the gel series for argon, series SF for nitrogen, series SC for cyclohexane, and series SC and SF for benzene. For the other systems investigated there are more pronounced variations, particularly when the constant \underline{c} in Eq. (1) changes appreciably as the result of chemical modification of the gel surface. The most striking example of this is provided by the adsorption isotherms for nitrogen shown in Fig. 1 of the second paper of this series [2]. According to this figure, the isotherm for the methylated gel S-1 lies considerably below that for the demethylated gel S-2. However, the constant \underline{c} in the isotherm Eq. (1) is 2.7 times as much with S-2 as with S-1. Consequently, according to the BET theory, the monolayers are filled at different relative pressures, namely, $h_m = 0.112$ for S-1 and $h_m = 0.072$ for S-2. The adsorptions corresponding to these pressures, interpolated from the isotherms, are 2.08 and 2.16 mMole/g respectively, and coincide exactly with the values of a_m . It is natural that the values of the adsorptions a_{h_m} for the mean relative pressure $h_m = 0.092$ differ significantly from the values of the constants a_m (Table 1).

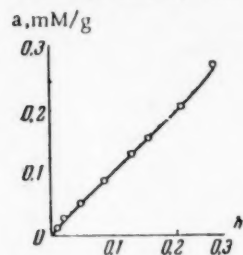


Fig. 1. The adsorption isotherm for cyclohexane vapor on silica gel SC at 20°. The continuous line is calculated from Eq. (1) with $a_m = 0.400$ mM/g and $c = 2.62$. The experimental points are denoted by circles.

The relative changes, produced by chemical modification, in the adsorptive capacities of the gels for nitrogen and argon vapors are practically the same for each series of gels. An idea of the effect of porous structure can be obtained by comparing changes in the relative values of the constant a_m of the absorption isotherm equation for different vapors, on characteristic samples of fluorine-substituted gels, namely, coarse pore SC-1 and fine pore SF-2 (Table 4).

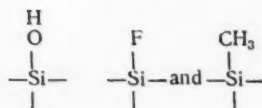
According to the data of Table 4, the relative values of a_m are practically the same for the two gels. They are also the same for water vapor. In all these cases there is practically no effect of the increased adsorption potential in the finer pores of gel SF-2. However, a marked effect has been reported previously with cyclohexane and benzene vapors on SF-2 [4]. The relative values of a_m for organic vapors are, indeed, considerably higher for SF-2 than for the coarse porous SF-1. Qualitatively similar conclusions result from a comparison of the affinity coefficients of the isotherms

2. In order to obtain a qualitative understanding of the main reasons for the decrease in adsorptive capacity of silica gel as the result of chemical modification, we carried out some approximate calculations of the dispersive interaction constants, C (Kirkwood [5]), and of the functions C/r^3 , which determine the energy of dispersive interaction, φ_D , of adsorbed molecules with a uniform adsorbent surface:

$$\varphi_D = -A(C/r^3). \quad (3)$$

These calculations were carried out for the limiting cases of surfaces completely covered with hydroxyl groups, and for those with the hydroxyl groups completely replaced by fluorine atoms or CH_3 groups. Since we were only interested in relative changes in adsorption energy for the vapor of non-polar substances, we used the simple expression (3) for φ_D , obtained by integration. The qualitative character of our considerations made it possible to neglect all other forms of interaction in calculating this main component.

The functional groups of the silica gel surface for the three typical cases considered were:



The data of [6] and values calculated additively were used to obtain the polarizabilities, α , and the diamagnetic susceptibilities, χ , for the adsorbed molecules and the surface groups. Values of α and χ were calculated for the whole molecules $\text{Si}(\text{OH})_4$, SiF_4 , and $\text{Si}(\text{CH}_3)_4$, and quartervalues were then taken for the surface groups.

TABLE 4

Relative Values of a_m for Silica Gel Samples of Different Structural Porosity

Vapor	SC-1	SF-2	Vapor	SC-1	SF-2
N_2	0.85	0.85	C_6H_6	0.33	0.46
Ar	0.82	0.83	H_2O	0.37	0.38
C_6H_{12}	0.44	0.76			

The Van der Waals radii, r_1 , of the adsorbed molecules were taken from [6] (calculated from the critical constants), while the radii, r_2 , for the surface functional groups were taken as those of the end groups OH, F, and CH₃ [6, 7]. The Van der Waals radius of the OH group was assumed to be the same as r_1 for the water molecule. According to Fig. 73 of [7], this is very nearly correct. The equilibrium separation, r , was then taken as the sum of r_1 and r_2 :

$$r = r_1 + r_2 \quad (4)$$

TABLE 5
Data Used for Calculating Constants

	$\alpha \cdot 10^{24}, \text{cm}^3$	$-X \cdot 10^{30}, \text{cm}^3$	$r_1, \text{ and } r_2, \text{ \AA}$
N ₂	4.76	49.9	1.57
Ar	1.63	32.2	1.48
C ₆ H ₁₂	10.87	113.0	2.42
C ₆ H ₆	10.32	92.0	2.26
H ₂ O	1.46	17.4	1.45
$\begin{array}{c} \\ -\text{Si}-\text{OH} \\ \end{array}$	1.90	22.2	1.45
$\begin{array}{c} \\ -\text{Si}-\text{F} \\ \end{array}$	0.83	15.9	1.35
$\begin{array}{c} \\ -\text{Si}-\text{CH}_3 \\ \end{array}$	2.27	20.8	2.0

Table 5 shows the values of the constants and Van der Waals radii r_1 and r_2 used for the approximate calculation of the dispersive interactions constants, C , and of C/r^3 ; according to (3), the latter is proportional to the dispersive interaction energy, φ_D . Table 6 contains the results of these approximate calculations.

According to Table 6, the dispersive interaction constants for the fully fluorided gel are substantially lower than those for the gel with surface hydroxyl groups. This is associated with the low polarizability of the fluorine atom. However, methylation of the surface groups differs from fluoridation in producing no significant change in C . The last two columns of Table 6 show the relative values of the adsorption energies for the gels with chemically modified surface, the adsorption energies (due to dispersive interaction) for the gels with surface hydroxyl groups being taken as unity for each adsorbate. These

results show that the adsorption energies of the vapors under consideration are 30-45% higher for silica gels with OH groups than for those with surface F or CH₃ groups. In the case of the fluorided gel the main cause of the reduction in adsorptive capacity is the already-noted small value of the dispersive interaction constant, while for the methylated gel it is the relatively high Van der Waals radius of the CH₃ group.

TABLE 6
Constants and Relative Values of the Dispersive Interaction Energies

	$-C \cdot 10^{59}, \text{erg. cm}^6$			$-\frac{C}{r^3} \cdot 10^{25}, \text{erg. cm}^3$			Relative energies	
	$\begin{array}{c} \\ -\text{Si}- \\ \end{array}$ OH	$\begin{array}{c} \\ -\text{Si}- \\ \end{array}$ F	$\begin{array}{c} \\ -\text{Si}- \\ \end{array}$ CH ₃	$\begin{array}{c} \\ -\text{Si}- \\ \end{array}$ OH	$\begin{array}{c} \\ -\text{Si}- \\ \end{array}$ F	$\begin{array}{c} \\ -\text{Si}- \\ \end{array}$ CH ₃	$\begin{array}{c} \\ -\text{Si}- \\ \end{array}$ F	$\begin{array}{c} \\ -\text{Si}- \\ \end{array}$ CH ₃
N ₂	9.3	5.1	10.0	0.34	0.21	0.22	0.62	0.55
Ar	11.2	6.5	11.4	0.45	0.29	0.25	0.64	0.56
C ₆ H ₁₂	55.6	30.0	59.3	0.96	0.54	0.69	0.56	0.72
C ₆ H ₆	51.1	25.7	52.2	1.00	0.55	0.67	0.55	0.67
H ₂ O	8.1	4.4	8.5	0.33	0.20	0.21	0.61	0.64

The calculations for water show the small role of dispersive forces in the adsorption of its vapor. Indeed, the values of C/r^3 for nitrogen and water are very similar for all the model adsorbents. Consequently, water vapor is probably adsorbed by silica gels as the result of dispersive interaction to approximately the same extent as nitrogen at room temperature.

Thus, the approximate calculations give a reasonable basis for qualitative interpretation of the differences in adsorptive capacity between the initial gels with surface OH groups and the fluorided or methylated gels. However, quantitative relations will be rather different in practice, since nitrogen possesses a quadrupole moment which has not been considered. Moreover, no allowance has been made for the additional donor-acceptor interaction [8] in the cases of water and benzene, whereas this plays a definite role in the adsorption of water on adsorbents with surface OH groups. Consequently, the relative changes in adsorption energy and adsorptive capacity will be considerably greater for water and benzene than is shown in Table 6. Silica gels with partial replacement of hydroxyl groups, i.e., adsorbents with a chemically heterogeneous surface, will probably occupy an in-

intermediate position. In this case the surface heterogeneity itself can have a specific effect on the adsorption energy and adsorptive capacity of vapors, in association with the topography of the surface groups and the nature and dimensions of the adsorbed molecules.

3. Parallel to the decrease in adsorptive capacity as the result of chemical modification of the silica gel surface, it was observed that, particularly with organic vapors and water, there was a considerable reduction in the constant a_m of Eq. (1); on the BET theory this constant corresponds to the vapor adsorption for a completely filled monomolecular layer. However, replacement of surface OH groups by F or CH₃ groups did not produce any substantial decrease in the specific surface of a gel [1, 2]. The formal consequence of this is that there must have been a marked increase in the cross sectional area, ω , of the adsorbate in the filled molecular layer in accordance with the data in Table 6 of [1] and Table 4 of [2]. Such an increase in ω , amounting to 200-300% for water, would appear to be qualitatively quite natural for water molecules, since the latter are adsorbed by formation of hydrogen bonds between the adsorbed molecules and surface hydroxyl groups. It is obvious that the number of hydroxyl groups per unit surface of gel must have been considerably reduced by chemical surface treatment.

However, for cyclohexane and benzene the calculated molecular cross sectional areas are greater than their normal values by factors of 7-12 on the coarse porous gels of series SC and S. It is not very likely that a change in the value of ω can provide a reasonable explanation of this, except in the sense of a purely formal application of the BET adsorption isotherm equation. Since the adsorption of cyclohexane vapor provides the most anomalous picture, it is convenient to make the most detailed analysis of the system cyclohexane-coarse porous silica gel, SC.

For the experimental adsorption isotherm of cyclohexane vapor on silica gel SC at 20° it is sufficient to apply the adsorption isotherm Eq. (1) to the range of equilibrium relative pressure $h = 0.05$ to 0.25 . The calculated values of the equation constants are $a_m = 0.400$ mM/g and $c = 2.62$. The corresponding calculated and experimental values of the adsorption are shown graphically in Fig. 1. The small value of the constant c formally denotes a relatively weak interaction between the adsorbed molecules and the gel surface. In such a case the mutual interaction between the adsorbed molecules in the monomolecular layer must have a substantial influence on the adsorption. We have attempted a qualitative analysis to deduce how a tangential interaction together with a normal interaction will affect the value of the calculated constant a_m .

Kiselev has proposed a semiempirical equation for the adsorption isotherm, using a constant k'_1 to express the interaction between the adsorbed molecules and the adsorbent surface, assumed to be energetically homogeneous, and a constant k_n to express the mutual interaction between the adsorbed molecules in the monomolecular layer [9]:

$$h = \frac{\theta}{k'_1(1-\theta)(1+k_n\theta)}, \quad (5)$$

where θ is the degree of filling of the monolayer:

$$\theta = \frac{a}{a_m} \quad (6)$$

and h is the equilibrium relative pressure. The determined value of a_m can be used to calculate θ for any value of a , and Eq. (5) can then be solved graphically for k'_1 and k_n .

The specific surface for silica gel SC, derived from the low temperature isotherm of nitrogen vapor, is $S = 326$ m²/g (Table 3). According to [10], the molecular cross sectional area for C₆H₁₂ on a uniform graphite surface is 38 Å², and this is in agreement with the area calculated from the dimensions of molecules located parallel to the surface (39 Å²). Taking the value $\omega = 38$ Å² as a physical constant of the molecule, then, for $s = 326$ m²/g, the value of the adsorption a_m for a continuous monomolecular layer should be $a_m = 1.43$ mM/g, and the experimental values of the adsorption will be (as for $a_m = 0.400$ mM/g) in the region of monomolecular filling of the gel surface. The value of θ is then calculated from Eq. (6) with $a_m = 1.43$ mM/g. Eq. (5) is then used to calculate the adsorption isotherm for C₆H₁₂ vapor on silica gel SC, over the relative pressure range $h = 0.19-0.40$, with $k'_1 = 0.52$ and $k_n = 3.80$. Fig. 2 compares the Eq. (5) isotherm with the experimental points.

The isotherm calculated from Eq. (5) shows slight curvature. The experimental points at the lower end of the isotherm lie somewhat above the curve; a possible explanation for this is surface heterogeneity of the gel. Thus, the experimental data for adsorption of cyclohexane vapor on silica gel SC can be represented approximately by Eq. (5), using a physically based value for the molecular cross sectional area of cyclohexane. That $k_n > k'_1$ follows qualitatively from the data in Table 5.

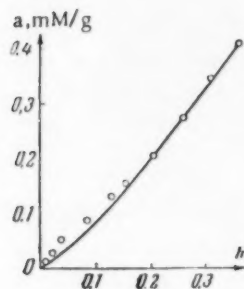


Fig. 2. The adsorption isotherm for cyclohexane vapor on silica gel SC at 20°. The continuous line is calculated from Eq. (5) with $a_m = 1.43$ mM/g, $k'_1 = 0.52$, and $k_n = 3.80$. The experimental points are denoted by circles.

Different values of k'_1 and k_n have also been used to calculate adsorption isotherms, and these have been analyzed in terms of the BET equation to determine the corresponding values of the constants a_m and c . It is only natural that the applicability of Eq. (1) is not particularly good, but it is sufficient to calculate the values of the constants. The results are shown in Table 7.

According to the data in Table 7, the application of the BET equation to the calculated adsorption isotherm leads to a substantial decrease in a_m , as compared with $a_m = 1.43$ mM/g used for calculating the initial isotherm. Increase in the constants k'_1 and k_n for the initial isotherm leads to an increase in the value of a_m derived from the BET equation. The relative values of a_m in the upper half of the table (1.00, 0.43, and 0.14) are, in general, close to those obtained for the SC silica gel series for adsorption of cyclohexane (1.00, 0.44, and 0.21, see Table 3). Thus, the result of carrying out this analysis is to give a picture of the formal applicability of the BET equation to those cases when the mutual interaction between the adsorbed molecules in the monolayer is comparable with their interaction with the adsorbent surface. This condition is qualitatively expressed by small values of the constants c in the BET equation. Similar calculations for C_6H_6 on SC show that, even with $c = 10$, the values determined for a_m indicate the presence of mutual interaction between the adsorbed molecules. Only when the constants for mutual adsorbate-adsorbate dispersive interaction are less than or do not significantly exceed the constants for adsorbate-adsorbent interaction, do the values of a_m approximate to the real values, suitable for calculating the specific surface of the adsorbent.

TABLE 7

Results of the Application of the BET Equation to the Adsorption Isotherms Calculated from Eq. (5) with $a_m = 1.43$ mM/g.

Isotherm calculated for		Derived from BET equation			ω, A^2 , calc. from a_m with $\omega_{N_2} = 16.2 A^2$
k'_1	k_n	a_m $\frac{mM}{g}$	c	Range of h	
0.52	3.80	0.525	1.77	0.14—0.40	103
0.26	3.80	0.227	1.70	0.07—0.34	239
0.13	3.80	0.075	1.54	0.08—0.45	724
0.52	3.80	0.525	1.77	0.14 —0.40	103
0.52	2.16	0.396	1.97	0.02 —0.30	137
0.52	0.52	0.245	2.92	0.025—0.30	221
0.52	0	0.240	3.20	0.02 —0.25	226
Experimental isotherm		0.400	2.62	0.07 —0.23	136

The author would like to thank A. V. Kiselev for discussing the results of the third section of this work.

SUMMARY

1. The main causes of the reduction in adsorptive capacity of silica gels for nonpolar vapors, as the result of replacement of surface hydroxyl groups by F atoms and CH₃ groups, are the changes in the dispersive interaction constants and Van der Waals radii of the surface groups, which determine the equilibrium distances between the adsorbed molecules in the surface monolayer.

2. This reduction in adsorptive capacity is greater when there is a substantial donor-acceptor component in the adsorptive interaction of the adsorbate.

3. Consideration has been given to the conditions for applicability of the Brunauer, Emmett and Teller adsorption isotherm equation for determination of the specific surface of an adsorbent.

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THE ACTIVITY OF CADMIUM OXIDE AS A CATALYST FOR HYDROGEN DEHYDROGENATION

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1751-1758, October, 1960

Original article submitted June 15, 1959

We show below that, on the basis of the experimental material for the dehydrogenation and dehydration of alcohols over oxides, it is possible to estimate the activities of these oxides for hydrocarbon dehydrogenation by calculating the activation energies for this latter process. We consider the oxides BeO, MgO, ZnO, and CdO. The value of ϵ_1 is calculated from the equation:

$$\epsilon_1 = \frac{2}{3} (\epsilon_2 + \epsilon_3) + Q_{OK} - 48,6, \quad (1)$$

obtained by solution of the system of equations of the multiplet theory [1]:

$$E_1 = -2Q_{CH} + 2Q_{CK} + 2Q_{HK} \quad (2)$$

$$E_2 = -Q_{CH} - Q_{OH} + Q_{OK} + 2Q_{HK} + Q_{CK} \quad (3)$$

$$E_3 = -Q_{CH} - Q_{CO} + 2Q_{CK} + Q_{HK} + Q_{OK} \quad (4)$$

$$\epsilon = -\frac{3}{4} E. \quad (5)$$

Here Q_{OH} , Q_{CO} , and Q_{CH} are the tabulated values of the mean bond energies [2] between the atoms in the reacting molecules; Q_{CK} , Q_{HK} , and Q_{OK} are the bond energies between these atoms and the catalyst; $-E_1$, $-E_2$, and $-E_3$ are the energy barriers, and ϵ_1 , ϵ_2 , and ϵ_3 are the activation energies, corresponding 1) to hydrocarbon dehydrogenation, 2) to alcohol dehydrogenation, and 3) to alcohol dehydration, under conditions such that these reactions are limited by the adsorption stage of formation of a doublet complex [1]. All these energy values are expressed in kcal/mole. If the reactions 1), 2), and 3) are two-stage [1], then the expressions for E_1 , E_2 , and E_3 are different, and Eq. (1) has the form:

$$\epsilon_1 = \frac{2}{3} (\epsilon_2 + \epsilon_3) - Q_{OK} + 59,3. \quad (6)$$

In order to calculate ϵ_1 from Eq. (1) for BeO, MgO, ZnO, and CdO, it is necessary to know ϵ_2 , ϵ_3 , and Q_{OK} for these oxides. We have used the values of ϵ_2 and ϵ_3 for isopropyl alcohol, found experimentally for these oxides by Krylov, Roginskii, and Fokina [3]. The bond energy Q_{OK} between the oxygen of the reacting molecule and the catalyst is taken as the mean energy of a single bond between the metal and oxygen, Q_{O-Me} (where Me is an atom of Be, Mg, Zn, or Cd), calculated by us thermodynamically [4-6]; Q_{O-Me} was obtained for all compounds of the types MeO and Me(OH)₂, and the results were averaged for each pair of MeO and Me(OH)₂ (Table 1). It should be noted that for all these oxides, as with Cr₂O₃ [7], the active centers for hydrocarbon dehydrogenation and for dehydrogenation and dehydration of alcohols are mainly the metal ions. If it is assumed that the active

centers are oxygen atoms, then $Q_{O-K} = Q_{O-O}$; however, the formation of peroxides under the conditions considered is extremely improbable from the chemical viewpoint.

TABLE 1

Calculation of ϵ_1 from ϵ_2 , ϵ_3 , and Q_{OK} (kcal/mole)

MeO catalyst	Q_{MeO} , heat of reaction $Me + O \rightarrow MeO$	$Q_{Me(OH)_2}$, heat of reaction $Me + 2OH \rightarrow Me(OH)_2$	Q_{O-Me} , energy of single bond			Method of preparing MeO	Experi- mental		Calcu- lated
			MeO	$Me(OH)_2$	Mean		ϵ_2	ϵ_3	
BeO	205,1	218,1	102,6	109,0	105,8	Ignition of carbonate	29,0	35,0	99,8
						Ignition of nitrate	21,0	35,0	94,6
						Precipitation from nitrate with NaOH	25,0	36,0	97,8
						Precipitation from $BeCl_2$	27,0	32,0	95,6
MgO	203	223,3	101,5	111,1	106,3	Precipitation from sulfate with NaOH	10,0	14,0	73,7
						Ignition of carbonate	28,0	32,0	97,7
						Precipitation from nitrate with NaOH	21,0	30,0	91,7
						Precipitation from nitrate with ammonia*	13,5	26,3	84,2
ZnO	142,3	154,8	71,1	77,4	74,2	Precipitation from sulfate with NaOH	13,0	26,0	51,6
						Precipitation from nitrate with NaOH	12,0	18,0	45,6
						Precipitation from nitrate with NaOH (another method)	13,0	18,0	46,2
CdO	120,0	134,6	60,0	67,3	63,6	Precipitation from nitrate with NaOH	10,0	24,0	39,6
						Precipitation from nitrate with NaOH (another method)	8,0	17,0	31,6
						Precipitation from nitrate with NaOH (another method)	11,0	19,0	35,0
						Decomposition of carbonate	14,0	24,0	40,4
						Decomposition of nitrate	16,0	24,0	41,6

* According to our experimental data

It follows from Table 1 that ϵ_1 is less affected by the method of preparation than by the nature of the catalyst; ϵ_1 decreases up the series BeO, MgO, ZnO, and CdO. The calculated values of ϵ_1 for BeO and MgO are of the same order of magnitude as the energies for rupture of the bonds C-H (90.5 kcal/mole) and C-C (66.2 kcal/mole), which indicates that it would be impossible to dehydrogenate hydrocarbons catalytically over these oxides. In fact, there is no information in the literature concerning BeO and MgO as catalysts for hydrocarbon dehydrogenation. We have also shown (Table 1), that MgO, prepared from the nitrate by precipitation with ammonia, readily dehydrogenates and dehydrates isopropyl alcohol at 313-395°, but does not dehydrogenate cyclohexane even at 550°. The value of ϵ_1 for ZnO, found from Eq. (1), is considerably less than ϵ_1 for BeO or MgO, and is close to the experimental values of ϵ_1 found for oxide catalysts. This is in agreement with [8], where it is shown experimentally that ZnO dehydrogenates certain hydrocarbons. The value of ϵ_1 calculated for CdO is even less than that for ZnO. This suggests that CdO should dehydrogenate hydrocarbons still more readily. The same conclusion emerges from a consideration of the position of the adsorption potential [1], q_1 , for the dehydrogenation of hydrocarbons on BeO, MgO, ZnO, and CdO (points of intersection) on the volcano-shaped curve. From Eq. (2), in which

$$2Q_{CK} + 2Q_{HK} = q_1, \quad (7)$$

it follows that

$$q_1 = E_1 + 2Q_{CH} \quad (8)$$

or, making use of (5), that

$$q_1 = 2Q_{CH} - \frac{4}{3} \epsilon_1 \quad (9)$$

The values of q_1 for BeO, MgO, ZnO, and CdO, calculated from Eq. (9) and the values of ϵ_1 from Table 1 are shown in Table 2 and Fig. 1. Values of q_1 for dehydrogenation of hydrocarbons by the oxides Cr_2O_3 , CeO_2 , ZrO_2 , and ThO_2 were calculated from Eq. (7), using bond energies found experimentally by the kinetic method [7, 9-11] and Cottrell's data for Q_{OH} , Q_{CO} , and Q_{CH} [2].

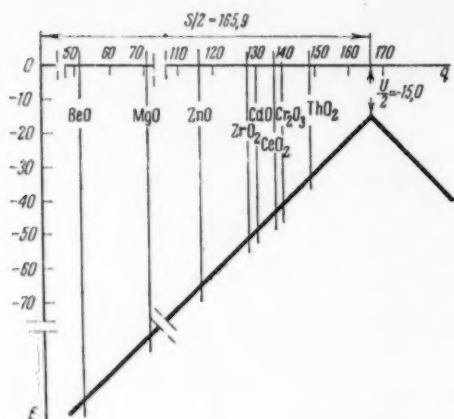


Fig. 1. Dependence of q_1 on the nature of the catalyst.

that hydrocarbons should dehydrogenate over ZnO and still more readily over CdO, and we resolved to confirm the latter experimentally.

TABLE 2

Adsorption Potentials, q_1 , for Different Oxides kcal/mole

Catalysts prepared by different methods	Adsorption potentials, q_1		
	Min.	Max.	Mean
q_1 calculated from Eq. (9)			
BeO	47.8	54.9	51.3
MgO	58.7	82.7	70.7
ZnO	112.2	120.2	116.2
CdO	125.5	139.0	134.3
q_1 calculated from Eq. (7)			
Cr_2O_3 [7]	129.0	151.0	140.0
CeO_2 [9]	-	-	138.2
ZrO_2 [10]	124.2	136.6	130.4
ThO_2 [11]	144.4	152.0	148.2

It is clear from Table 2 and Fig. 1 that q_1 for BeO and MgO are a long way from the summit of the volcano-shaped curve, but that q_1 for ZnO and specially for CdO lie in the region for cyclohexane dehydrogenation catalysts. Values of ϵ_1 , obtained from Eq. (6), vary from -7.0 to +12.0 kcal/mole in the series BeO, MgO, ZnO, and CdO. These low values indicate that a two-stage scheme is not applicable to reactions 1), 2), and 3), and, consequently, that these reactions are indeed single stage [1].

It must be noted that calculations of ϵ_1 by Eqs. (1) or (6) are only approximate. The main cause of imprecision is that the value of Q_{O-Me} is less on the catalyst surface than the value calculated thermodynamically. If, in the calculation of ϵ_1 , we use for Q_{OK} the mean energy of a single coordination bond between metal and oxygen and assume a constant coordination unsaturation of the metal atoms on the surface, then we find a lower value of ϵ_1 than when using Q_{O-Me} , but the order of the activation energies is unaltered. It is clear that the order of succession is more important than the absolute values of ϵ_1 , and this order is not affected by the above mentioned lack of precision. Thus, calculation shows

There is no account in the literature of any investigation of CdO as a catalyst for hydrocarbon dehydrogenation. Other catalytic properties of CdO have been little studied. It is known [3, 12-14] that CdO catalyzes the dehydrogenation and dehydration of various alcohols and the ketonization of acids. In these there is always a partial reduction of CdO to metal [3, 12-15] by hydrogen, alcohol, acid, ketone, or aldehyde.

Experimental

We prepared cadmium oxide from a 15% solution of $Cd(NO_3)_2$ (pure for analysis) by precipitation with a 15% solution of ammonia in water at room temperature. The hydroxide was washed free of NO_3^- by decantation with 200 l of distilled water. The $Cd(OH)_2$, containing traces of NO_3^- , was shaped and dried at 110°. Complete removal of NO_3^- was achieved by dehydrating the $Cd(OH)_2$ at 300° and subsequently heating the CdO in a catalyst tube, at 500°, in a stream of CO_2 -free air. The cadmium

oxide was tabletted under a pressure of 150 atm, and crushed to 0.5 to 1 mm size. X-ray diffraction showed that the CdO was crystalline.

Experiments were carried out in a flow system, using the automatic apparatus [16-20] for studying catalytic reactions developed in our laboratory. A differential thermocouple was used for following thermal processes in the catalyst. Oxygen-free nitrogen was passed through the catalyst tube before and after experiments. The catalyst was regenerated in air between experiments. The physical constants of the starting materials agreed with literature values. The feed rate for liquids was 0.23 ml/min, and for gases 10.0 ml/min at N.T.P. The volume of each portion of catalyst was 4.6 ml, its weight 9.2 g, and the length of the bed 25 mm.

Cyclohexane Conversion was investigated in the range 458-540° (Table 3, A). Conversion was inconsiderable up to 487° (the thermal effect was practically nil), but benzene, cyclohexane, and water were detected qualitatively in the catalyzate. Conversion increased between 487 and 522°. There were no gaseous products. A deposit formed in the cold part of the tube, and this was shown by a qualitative test [21] to be cadmium. Thus, CdO was reduced to metal during the reaction; part of this metal evaporated and deposited in the cold part of the tube, but part of it alloyed with the thermocouple metal and strongly affected the total emf, so that the differential thermocouple was a sensitive indicator for the process of catalyst reduction.

TABLE 3

A. Conversion of Cyclohexane over CdO

Temp. °C	Catalyzate composition, % w/w				Conversion of feed, mole % to		m, vol. gas pro- duced, ml/min N. T. P.	Composition of gas products, % v/v		
	C ₆ H ₁₂	C ₆ H ₁₀	C ₆ H ₆	H ₂ O	C ₆ H ₁₀	C ₆ H ₆		C _n H _{2n±2}	C _n H _{2n}	CO ₂
457	~100,0	Traces								
475	~100,0	"								
487	89,0	1,8		4,0	1,9	6,1				
495	76,1	2,5	12,3	9,1	2,8	14,5				
510	81,1	2,9	9,1	6,9	3,2	10,4				0,3
522	72,1	3,1	14,3	10,5	3,6	17,0				0,4
530		12,3	15,0	Cracking			2,1	68,3	28,5	3,2
550		21,7	19,3	"			6,7	43,8	50,1	6,1
522	~100,0	Catalyst completely reduced					—	—	—	—

B. Conversion of Cyclohexene over CdO

450		100,0	Traces							
470		88,3	7,8	3,4		8,7				
485		73,5	19,4	8,5		21,6				0,3
500		74,6	17,1	7,5		19,3				0,4
510		70,3	20,3	8,8		23,0				0,3
519,5			24,9	Cracking			4,1	52,3	46,1	1,6

Cyclohexane was isolated as an addition product with adipic acid [22], benzene was detected by its reaction with antimony chloride in carbon tetrachloride [23], and water was detected by its reaction with anhydrous CuSO₄. Cyclohexene was determined by means of its bromine number. Since water, cyclohexene, and benzene were formed by reactions I or II (see discussion of results), it was possible to determine the benzene from the quantities of water and cyclohexene formed; the cyclohexene was determined, before and after removal of water with potash, so that the total water could be corrected for that formed by the production of cyclohexene. Benzene and cyclohexane were also determined from the refractive index of the catalyzate, after removing cyclohexene as a mercury derivative [23] and water with potash; the water content could be calculated from the quantities of benzene and cyclohexene. The benzene and cyclohexene contents did not increase very much at higher temperatures owing to reduction of the catalyst and consequent loss of activity. Metallic cadmium did not dehydrogenate cyclohexane (Table 3, A).

Cyclohexene Conversion to benzene was investigated between 470 and 520° (Table 3, B). Under similar conditions cyclohexane was converted to benzene in poor yield. Cyclohexadiene was not detected in the catalyzate. The reverse action did not occur, since no cyclohexane was found in the catalyzate; the total content of cyclohexene, water, and benzene amounted to ~ 100%. The reaction products were identified as described above.

Butene Conversion to butadiene was investigated between 575 and 605° (Table 4) in a nitrogen atmosphere. The maximum conversion was 5.6%. The reaction products contained up to 2.7% of CO₂.

TABLE 4
Conversion of Butene over CdO

Temperature, °C	Composition of gaseous products, % v/v			Conversion of feed, mole %
	Butene	Butadiene	CO ₂	
560	—	—	—	—
575	97,8	1,9	0,3	1,9
585	97,5	2,1	0,4	2,1
593	92,2	5,4	2,4	5,5
605	91,8	5,5	2,7	5,6

Piperidine Conversion to pyridine was investigated between 465 and 520° (Table 5). Pyridine was detected in the catalyzate by its reaction with CdCl₂ [23], piperidine by decolorization of a weak permanganate solution [24], and piperidine by its reaction with sodium nitroprusside and acetaldehyde [25]. Pyridine distilled in steam was isolated as picrate [23, 24] of m.p. 164°. The composition of the catalyzate was determined from the refractive index of the piperidine-pyridine mixture (water was first removed). The variation of n_D^{20} with composition was nearly linear [24]. The analysis was affected by the piperidine, present to the extent of a few percent of mixed isomers. The analytical results indicated that piperidine was converted to pyridine via piperidine.

TABLE 5
Conversion of Piperidine over CdO

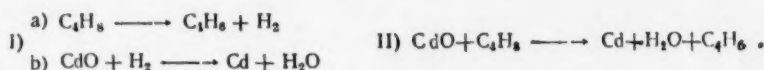
Temp. °C	n_D^{20} of dried catalyzate	Pyridine in catalyzate % w/w	Conversion of feed, mole %	m. vol. gas produced, ml/min N. T. P.	Composition of gaseous products, % v/v		
					Hydrocarbons		CO ₂
					Sat.	Unsat.	
465	1,4515	—	—	—			
470	1,4517	Traces	—	—			
481	1,4527	2,2	2,5	—			
493	1,4539	5,1	5,6	—			
505	1,4590	13,2	14,6	—			0,8
520	1,4580	11,4	12,7	—			0,7
531	1,4679	24,6	Cracking	5,4	23,6	73,1	3,4

Methane was not reduced by CdO between 500 and 595°; this was shown by use of the differential thermocouple and by gas analysis. Reduction of CdO by carbon, produced by partial cracking of the hydrocarbon used, is thermodynamically possible, but was negligible up to 600°; there was hardly any CO₂ in the gaseous products (Tables 3-5), and CdCO₃ is not formed above 450° [25].

Thus, the conversions of cyclohexene, butene, and piperidine over CdO were analogous to that of cyclohexane. The catalyzates contained the corresponding dehydrogenation products and water; the catalyst was reduced to metal and hydrogen was not evolved.

Discussion of Results

Analysis of the experimental results showed that two types of reaction occurred: (I) catalytic dehydrogenation over CdO and reduction of the catalyst by hydrogen, and (II) the single stage reduction of CdO by the feed material. In the case of butene these reactions may be written:



This conclusion is in agreement with the following data:

1. It has been shown [14] that, when isopropyl or ethyl alcohol is dehydrogenated catalytically over CdO, there is partial reduction of the catalyst by the alcohol and by the hydrogen obtained. According to thermodynamic calculations, under the conditions for dehydrogenating hydrocarbons, CdO should be still more easily reduced by hydrogen, and hydrogen was entirely absent from the gas phase in our experiments. In our case the existence of a catalytic reaction was not shown directly (by hydrogen formation), but its possibility cannot be excluded.

2. Reaction II is thermodynamically identical with reaction I, but Ia is not the same as II. We calculated K_p for these reactions at different temperatures (427-605°) for all the substances investigated. The results showed that in all cases, except for the reaction butene \rightarrow butadiene, the reaction should be completely displaced to the right, although K_p for reaction Ia is less than for reaction II by 2-4 orders of magnitude. Under the conditions of a flow system, in consequence of the high volatility of cadmium [6], there is a possibility that it may be formed directly in the vapor state. In this case, for butene and piperidine, K_p for reaction II differs very little from K_p for reaction Ia, and the difference is only one order of magnitude for cyclohexane and cyclohexene. Thus, the calculated values of K_p indicate approximately the same thermodynamic probabilities for reactions Ia and II.

3. The experimental and calculated results show clearly that reaction I always accompanies reaction II. The conversions were investigated first at temperatures normal for catalytic dehydrogenation over oxides. The reaction products contained the substances normally obtained by catalytic dehydrogenation of the starting materials. Methane cannot be dehydrogenated catalytically and did not reduce CdO, although such reduction is thermodynamically possible to a considerable extent, even at 520°. In consequence of the high (23.6 kcal/mole) energy of the bond between cadmium and carbon, calculated from thermodynamic data [26], hydrocarbons are evidently adsorbed on CdO by the grouping



and not only by two hydrogen atoms. Such adsorption is energetically more favorable. This view is confirmed by our observation that the heat of adsorption of the feed material was greater than the heat of adsorption of H_2 . As a result of this, both the C-H bonds are considerably weakened, and this can lead to a splitting off of hydrogen (i.e., to a catalytic reaction) which combines with part of the oxygen directly bonded to Cd. Thus, the old catalytic centers are gradually destroyed, but can be newly formed.

Summary

1. The capabilities of BeO, MgO, ZnO, and CdO for dehydrogenating hydrocarbons were estimated on the basis of the multiplet theory. The calculations showed that ZnO and CdO should catalyze reactions of this type, but that BeO and MgO should not.

2. It was found experimentally that CdO dehydrogenated cyclohexane, cyclohexene, piperidine, and butene, and that the catalyst was simultaneously reduced to the metal by the hydrogen from the feed material.

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THE RATE OF THERMAL DECOMPOSITION OF ETHANE UNDER EQUILIBRIUM CONDITIONS AND FAR AWAY FROM EQUILIBRIUM

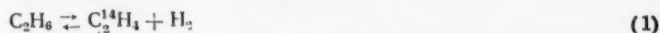
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1759-1762, October, 1960

Original article submitted June 4, 1959

The kinetic method [1] of using labeled atoms makes it possible to solve the quite difficult problem of determining separately the rates of the forward and reverse reactions in reversible processes. We have studied the reversible reaction of thermal decomposition of ethane:



under conditions of equilibrium at 600 and 554°. Equilibrium mixtures of ethane, hydrogen, and ethylene labeled with radioactive carbon C^{14} , were introduced into a 725 ml capacity quartz reaction vessel, at 142 mm Hg pressure at 600° and at 146 mm pressure at 554°. The compositions of the equilibrium mixtures are shown in Table 1.

TABLE 1

Compositions of the Equilibrium Mixtures in Experiments to Investigate the Reaction $\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$

Pressure, mm, Hg.	Temperature, °C	
	600	554
P_{total}	142	146
$P_{\text{C}_2\text{H}_6}$	70	100
$P_{\text{C}_2\text{H}_4}$	36	23
P_{H_2}	36	23

Although the pressure remained constant in this equilibrium system, yet all the time two opposite processes were occurring with equal speeds, namely, the consumption and formation of each component. Thus, by using chromatography [2] to analyze the reaction products, and by measuring the specific activities of the ethane and ethylene, we could measure the rate of accumulation of $\text{C}_2^{14}\text{H}_6$ or the rate of disappearance of $\text{C}_2^{14}\text{H}_4$, and hence determine the rate of the forward reaction in the equilibrium system [1]. Figs. 1 and 2 show the changes in specific activities of ethylene and ethane with time, under equilibrium conditions, at 600 and 554°. The specific activity is expressed in $\mu\text{C}/\text{mM}$ of gas. In balancing the activities between the initial and final products, we normally obtained differences of 3-6%, and only in a few cases did these differences amount to 10-15%. The activity balances of the products are shown in Tables 2 and 3.

The rate of formation of ethylene, i.e., the rate of the forward reaction in an equilibrium system [1], was obtained by the kinetic method from the equation:

$$w_{\text{equil}} = \frac{[\text{C}_2\text{H}_6]}{\beta - \alpha} \frac{d\alpha}{dt}; \quad (2)$$

where α is the specific activity of the ethane and β the specific activity of the ethylene. Values of w_{equil} , obtained by this method for 600 and 554°, are shown in Tables 4 and 5.

It is apparent from Tables 4 and 5 that the values of w_{equil} did not remain constant, but decreased somewhat with time. This was probably associated with the formation of secondary products [3] (methane, propene, and

and higher hydrocarbons) in the course of the reaction, so that the values for w_{equil} , obtained at the start, in the absence of secondary products, are to be preferred.

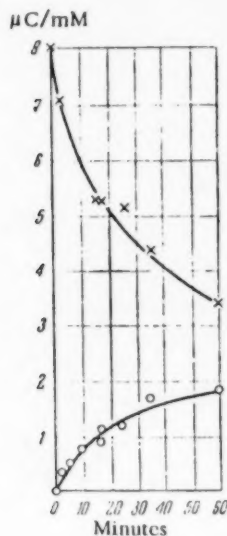


Fig. 1.

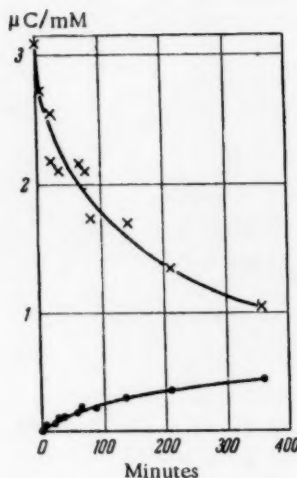


Fig. 2.

In 1956 Voevodskii [4] suggested a method of indicating chain reactions in reversible processes. This author considered that the high speed of chain processes was associated with the formation of a more-than-equilibrium concentration of radicals in such processes. Thus, in the case of a chain reaction



(3)

TABLE 2

Activity Balance Between Initial and Final Products ($T = 600^\circ\text{C}$).

τ_{min}	$\text{I}_{\text{C}_2\text{H}_6}, \mu, \text{C}$	$\text{I}_{\text{C}_2\text{H}_4}, \mu, \text{C}$	$\Sigma \text{I}, \mu, \text{C}$	$\frac{\Sigma \text{I}}{I_0} 100\%$
0	0	3,8	3,8	100
3	0,3	3,4	3,7	97
10	0,7	2,9	3,6	95
16	0,9	2,5	3,4	90
17,5	1,0	2,5	3,5	92
25	1,2	2,5	3,7	97
35	1,6	2,1	3,7	97
60	1,7	1,6	3,3	87

TABLE 3

Activity Balance Between Initial and Final Products ($T = 554^\circ\text{C}$).

τ_{min}	$\text{I}_{\text{C}_2\text{H}_6}, \mu, \text{C}$	$\text{I}_{\text{C}_2\text{H}_4}, \mu, \text{C}$	$\Sigma \text{I}, \mu, \text{C}$	$\frac{\Sigma \text{I}}{I_0} 100\%$
0	0	1,07	1,07	100
5	0,07	0,95	1,02	96
20	0,11	0,88	0,99	93
30	0,16	0,75	0,91	85
40	0,19	0,72	0,91	85
60	0,24	0,73	0,97	91
70	0,29	0,72	1,01	95
90	0,30	0,60	0,90	84
140	0,42	0,58	1,00	94
210	0,52	0,46	0,98	92
360	0,65	0,35	1,00	94

the concentration of at least one of the radicals under equilibrium conditions $[\text{R}_i]_{\text{equil}}$ should be less than the concentration of the same radical under conditions remote from equilibrium $[\text{R}_i]$:

$$[\text{R}_i]_{\text{equil}} < [\text{R}_i] \quad (4)$$

It is well known that it is difficult to measure the absolute concentrations of radicals in the course of a reaction. However, if it is accepted that the reaction velocity provides a measure of the concentration of free radicals during a chain process, then a comparison of the reaction velocities [3] at equilibrium and remote from equilibrium

$$w_{\text{equil}} < w,$$

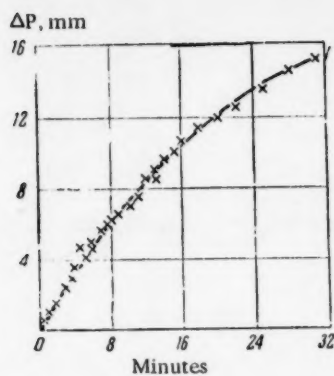


Fig. 3.

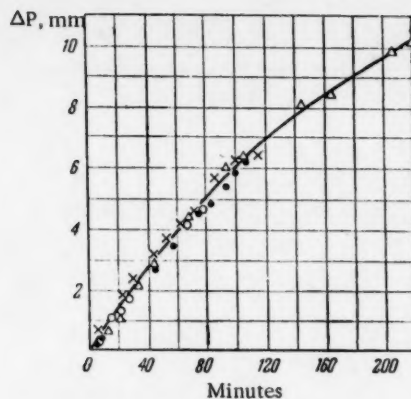
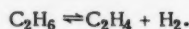


Fig. 4.

should provide an indication of a chain reaction mechanism. To check this experimentally, we used the reaction:



As described above, the rate of the forward reaction, $w_{\text{equil.}}$, for such a system was determined with the aid of labeled ethylene. We also determined the rate of decomposition of pure ethane in the absence of ethylene and hydrogen. This ethane was subjected to thermal decomposition under the same conditions as were used for investigating the equilibrium reaction (1). The initial ethane pressure, p_0 , in the reaction vessel was made equal

TABLE 4

The Rate of Decomposition
of Ethane under Equilibrium
Conditions $\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2^{14}\text{H}_4 + \text{H}_2$
($T = 600^\circ\text{C}$)

τ min	$w_{\text{equil.}}$, mm Hg/min
10	0,66
15	0,62
20	0,55
25	0,56
30	0,53

TABLE 5

The Rate of Decomposition
of Ethane under Equilibrium
Conditions $\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2^{14}\text{H}_4 + \text{H}_2$
($T = 554^\circ\text{C}$)

τ min	$w_{\text{equil.}}$, mm Hg/min
45	0,096
60	0,094
90	0,095
120	0,088
150	0,081
180	0,083
210	0,085

to the partial pressure of ethane, $p_{\text{C}_2\text{H}_6}$, in the equilibrium

mixture. Figs. 3 and 4 show the kinetic curves for ethane

decomposition at 600 and 554°. Rates of ethane decomposition, w , in the absence of end products were obtained from the initial parts of these curves. Table 6 compares our results for the rates of ethane decomposition at equilibrium and remote from equilibrium.

TABLE 6

Comparison of the Rates of Ethane Decomposition at Equilibrium, $w_{\text{equil.}}$, and Remote from Equilibrium, w .

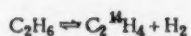
	p , mm Hg/min.	
	at 600°	at 554°
$w_{\text{equil.}}$	0,66	0,096
w	0,75	0,07

We have seen that for chain reactions $w_{\text{equil.}} < w$. According to our experiments, $w_{\text{equil.}} < w$ at 600° and $w_{\text{equil.}} > w$ at 554°. Thus, within the limits of accuracy of the measurements, we can say that, for the particular reaction studied, $w_{\text{equil.}} \approx w$. However, the thermal decomposition of ethane is undoubtedly a chain reaction, so we must conclude that the Voevodskii criterion is not sensitive enough to establish that this process has a chain mechanism.

In conclusion, we would like to thank V. V. Voevodskii for his interest and discussion of our work.

Summary

1. The kinetic labeled atom method has been used to measure the rate of the forward reaction of the process of ethane dehydrogenation:



under equilibrium conditions at 600 and 554°.

2. It is difficult to identify a chain mechanism of a reaction by comparing the reaction velocities in the absence of end products and under equilibrium conditions.

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THE KINETICS OF HEAT EVOLUTION IN THE THERMAL DECOMPOSITION OF TETRYL

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1763-1766, October, 1960

Original article submitted June 2, 1959

Measurement of heat evolution is one of the principal methods of investigating the kinetics of various types of chemical reaction. The application of this method to explosives, together with other methods of investigating decomposition kinetics (gas evolution and loss in weight), makes it possible to establish the character of the explosive decomposition reaction, the existence of separate stages in the process, the thermal stability of the explosive and the effect on this of different impurities, and to measure quantitatively the effects of additives on the decomposition. It is also very important to know the heat of thermal decomposition in order to calculate the critical conditions for thermal explosion, since the heat evolved in slow thermal decomposition leads to an increase in the temperature of the system, and finally to an explosion. There is no experimental data in the literature on such heats of thermal decomposition.

We, therefore, undertook some work on the direct investigation of the heats of decomposition of explosives and the kinetics of heat evolution in the decomposition process. A differential calorimeter was used, with automatic control as previously described [1]. This instrument enabled us to avoid the main difficulties arising in measuring thermal effects of slow reactions. With this type of calorimeter it was also possible to obtain directly the rate of heat evolution as a function of time, which was convenient for calculating the kinetic characteristics of the decomposition reactions of explosives.

The first material selected for investigation was tetryl, $[C_6H_2(NO_2)_3N(CH_3)NO_2]$, the kinetics of whose thermal decomposition have been adequately studied by a number of authors [2]. The composition and kinetics of accumulation of the gaseous and condensed products of the thermal decomposition of tetryl have also been investigated [3]. In our experiments, the rate of heat evolution of the decomposition reaction was investigated over the temperature range 130-155°. A sample weight was taken such that the rate of heat evolution in the calorimeter did not exceed 20 cal/hr. For example, 0.15 g was taken at 155° and 0.8 g at 130°. With such small samples, the temperature difference between the calorimeter block and the thermostat was never more than 0.2°, and the temperature difference between the substance in the ampoule and the thermostat, directly measured with a copper-constantan differential thermocouple, did not exceed 0.5°. Under these conditions the decomposition of tetryl in the calorimeter could be considered as isothermal.

The measure of the rate of heat evolution in the differential calorimeter was the power supplied by an electric current passing through a fixed resistance (R) heater in the reference block. If the temperatures and cooling constants of both blocks were the same,

$$dQ/dt = 0.239 I^2 R \text{ cal/sec} = 861 I^2 R \text{ cal/hr.} \quad (1)$$

The inertia of the apparatus was about 5 min; this was determined by passing electric currents through heaters in both blocks of the calorimeter. Since this inertia made it impossible to maintain exact uniformity of temperature at every instant of time, the current strength was altered in steps so as to give the experimental curve in the form of separate points.

Rate curves for the heat evolution in the thermal decomposition of tetryl (calculated back to 1 g of sample), for the temperature range 130-155°, are shown in Fig. 1. It is obvious that the decomposition is self-accelerating. For instance, at 155° the rate of heat evolution from an original 1 g of explosive alters from 30 cal/hr at the start to a maximum of 112 cal/hr, while at 130° it increases similarly from 1.8 to 7.5 cal/hr. The total heat of decomposition was obtained by integrating the rate curve. Total heats of thermal decomposition of tetryl over the temperature range studied are shown in Table 1.

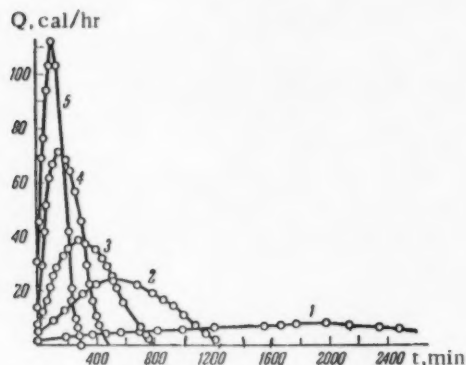


Fig. 1. Kinetic curves of heat evolution at various temperatures: 1) 130°, 2) 140°, 3) 145°, 4) 150°, 5) 155°.

The observed kinetics for tetryl decomposition could be represented by the equation for an autocatalytic reaction of the first order with a correction for the change in volume of the explosive during the reaction [4]:

$$\frac{d\eta}{dt} = k_1(1 - \eta) + k_2\alpha(1 - \mu) \cdot \frac{\eta \cdot (1 - \eta)}{1 - \mu \cdot \eta}, \quad (2)$$

where $\mu = (V_{\text{initial}} - V_{\text{final}})/V_{\text{initial}}$ is the fractional change in volume of the condensed phase at the end of the decomposition; for tetryl $\mu = 0.23$ (between 130 and 155°); k_1 is the velocity constant of the first order reaction; k_2 is the velocity constant of the catalytic reaction; α is the fraction of catalyst in the condensed reaction products; η is the extent of decomposition determined by the ratio of the amount of heat liberated up to a given moment to the total heat of reaction, i.e.,

$$\eta = \frac{\int_0^t \frac{dQ}{dt} \cdot dt}{\int_0^\infty \frac{dQ}{dt} \cdot dt} \quad (3)$$

It follows from (2) that $W_{\text{sp}} = \frac{1}{1 - \eta} \cdot \frac{d\eta}{dt}$ should be directly proportional to $\eta/(1 - \mu\eta)$. Fig. 2 shows this relation. It is clear that the specific velocity does increase linearly with $\eta/(1 - \mu\eta)$. The constants k_1 and $k_2\alpha \cdot (1 - \mu)$ in Eq. (2), as calculated from the experimental data, are shown in Table 1.

TABLE 1

Temp. °C	$k_1 \cdot 10^3$, min^{-1}	$k_2\alpha(1 - \mu)$ $\cdot 10^3$, min^{-1}	Q, cal/g	Temp. °C	$k_1 \cdot 10^3$, min^{-1}	$k_2\alpha(1 - \mu)$ $\cdot 10^3$, min^{-1}	Q, cal/g
155	2,44	16,4	341	145	1,02	5,50	338
155	2,42	13,6	342	145	0,94	5,15	330
155	2,80	14,5	345	145	0,97	4,35	349
150	1,54	9,9	350	145	0,90	4,76	345
150	1,42	9,0	343	140	0,54	3,30	348
150	1,43	10,2	329	130	0,16	0,93	327
145	0,98	5,15	337				

Since, in the overwhelming majority of cases, the kinetics of thermal decomposition of explosives, and particularly of tetryl, have been investigated by the gas evolution or loss in weight methods, it was of interest to compare this previous data with the results from heat evolution kinetics. The rate of tetryl decomposition greatly depends on the ratio of the sample mass to the reaction vessel volume [3], so that the comparison should be carried out under uniform conditions. Our experiments were carried out in closed vessels, so that, for comparison,

we also measured the kinetics of tetryl decomposition by the loss in weight method in closed vessels. The velocity constants, calculated from Eq. (2) for these later experiments, are shown in Table 2.

TABLE 2

Temp. °C	$k_1 \cdot 10^3$, min ⁻¹	$k_2 \alpha (1 - \mu)$, 10 ³ , min ⁻¹	Temp. °C	$k_1 \cdot 10^3$, min ⁻¹	$k_2 \alpha (1 - \mu) \cdot 10^3$, min ⁻¹
151	2.37	9.2	143	0.91	4.31
151	1.95	10.2	143	0.98	4.38
147	1.17	6.4	139	0.66	2.63
147	1.30	6.7	139	0.62	2.88
147	1.30	6.3	135	0.37	1.67

Figure 3 shows the temperature variation of the velocity constants for tetryl decomposition determined by the heat evolution and loss in weight methods. It is clear that the velocity constants determined by the two methods lie on lines which coincide within experimental error. Activation energies and pre-exponential factors were calculated from the slopes of these lines:

$$k_1 = 10^{16.6} \cdot e^{-\frac{36000}{RT}} \text{ min}^{-1}$$

$$k_2 \alpha (1 - \mu) = 10^{17.4} \cdot e^{-\frac{38000}{RT}} \text{ min}^{-1}$$

Thus, investigation of the kinetics of heat evolution in the thermal decomposition of tetryl showed that kinetic data obtained by different methods was mutually self consistent to a high degree of accuracy. The existence of an initial state in the decomposition, shown by investigation of the relation between rate of decomposition and the value of m/v [3], was confirmed by the existence of deviations from the simple linear relation

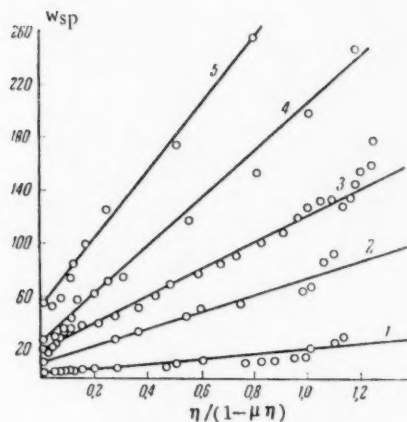


Fig. 2. Variation of W_{sp} with $\eta/(1 - \mu \eta)$:
1) 130°, 2) 140°, 3) 145°, 4) 150°, 5) 155°.

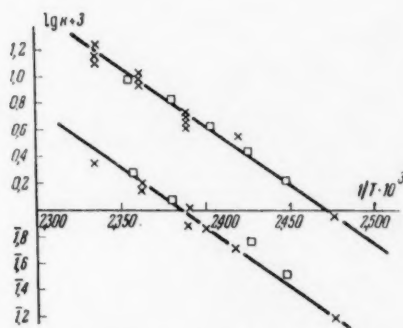


Fig. 3. Variation of $\log k$ with $1/T$ for the monomolecular and autocatalytic reactions.

between specific rate and $\eta/(1 - \mu \eta)$ at the start ($\eta \sim 0.1$). Some increase in the specific rate of decomposition towards the end of the process was associated with a slow reaction of decomposition of the residue (trinitroanisole and N-methyltrinitroaniline). This was in full agreement with analysis of the decomposition products, which were mainly picric acid and trinitroanisole; the observed heat of decomposition was 341 cal/g, a little less than the heat of explosion.

Summary

1. The kinetics of heat evolution for tetryl decomposition were measured over the temperature range 130-155°. The mean heat of reaction in this temperature range was 341 cal/g.
2. The kinetics of tetryl decomposition could be expressed by the equation for an autocatalytic reaction of the first order, with a correction for the change in volume during the reaction.
3. The calculated kinetic constants, pre-exponential factors, and activation energies for tetryl decomposition, over the temperature range studied, were the same, using data obtained by the heat evolution and loss in weight methods.

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SYNTHESIS OF HETEROCYCLIC COMPOUNDS HAVING PHOSPHORUS IN THE RING

COMMUNICATION 1. SYNTHESIS OF DERIVATIVES OF 1,2-OXAPHOSPHORINANE and 1,4,2-DIOXAPHOSPHORINANE 2-OXIDES

B. A. Arbuzov and D. Kh. Yarmukhametova

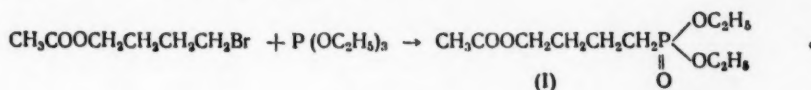
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1767-1771, October, 1960

Original article submitted May 11, 1959

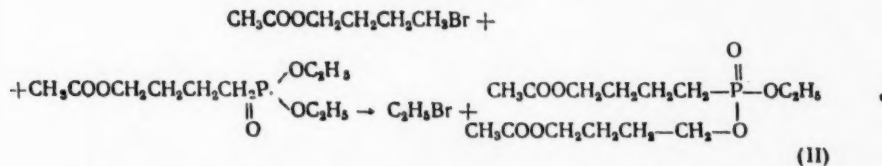
There has recently been a considerable increase in interest in cyclic phosphorous and phosphonic esters containing a heterocyclic ring having two oxygen atoms and a phosphorus atom. Many heterocyclic compounds containing a phosphorus atom linked with a carbon atom and an oxygen atom in the ring have been described. In various papers [1-5] it has been suggested that such heterocycles may exist as intermediate products. In a patent, Smith [6] refers to the preparation of this type of compound by the elimination of water from γ - and δ -hydroxyalkyl-phosphonic acids. There is a certain analogy between the phosphono and carboxy groups. It may therefore be expected that γ - and δ -hydroxy phosphonic acids, like γ - and δ -hydroxy carboxylic acids, will give compounds analogous to lactones. Szmuszkovicz [7] showed recently that derivatives of 3-(3-indolyl)-3-oxopropylphosphonic acid exist in a lactone form in the crystalline state, which confirms the analogy between carboxylic and phosphonic acids.

The present paper reports on the synthesis of phosphonic derivatives analogous to lactones formed by intramolecular cyclization by a transesterification reaction. By the action of 4-bromobutyl acetate on triethyl phosphite we prepared diethyl 4-acetoxybutylphosphonate (I):

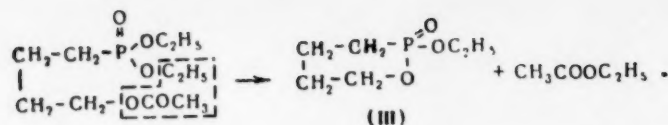


In addition to the expected product (I) we isolated a little of a compound which was found to be 4-acetoxybutyl ethyl 4-acetoxybutyl-phosphonate (II).

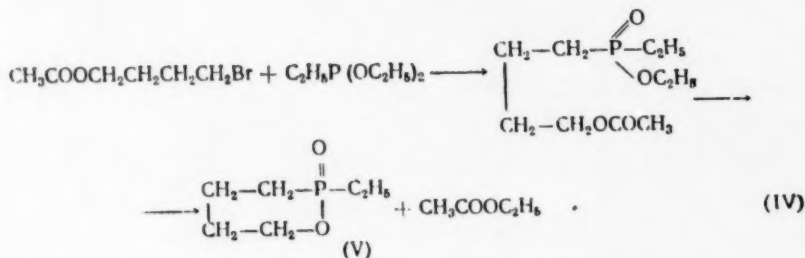
This substance is evidently formed by the action of 4-bromobutyl acetate on diethyl 4-acetoxybutylphosphonate:



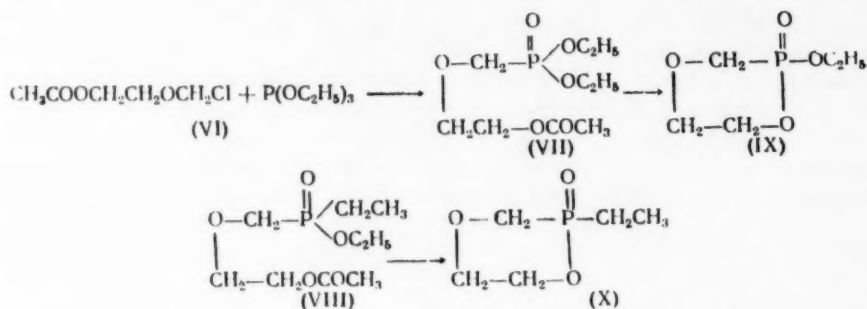
When (I) is heated with a little phosphoric acid as catalyst, cyclization occurs with elimination of ethyl acetate and formation of the cyclic ester (III) (2-ethoxy-1,2-oxaphosphorinane 2-oxide) [8]:



Similarly, by the action of 4-bromobutyl acetate on diethyl ethylphosphonite we obtained ethyl (4-acetoxybutyl)ethylphosphinate (IV), and elimination of ethyl acetate from this gave 2-ethyl-1,2-oxaphosphorinane 2-oxide (V):



In the same way by the action of 2-acetoxyethyl chloromethyl ether (VI) on triethyl phosphite and on diethyl ethylphosphonite we obtained the corresponding phosphonic and phosphinic esters (VII) and (VIII):



Elimination of ethyl acetate from (VII) gave 2-ethoxy-1,4,2-dioxaphosphorinane 2-oxide (IX), and elimination of ethyl acetate from (VIII) gave 2-ethyl-1,4,2-dioxaphosphorinane 2-oxide (X).

TABLE 1

Formula	B. p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR		Yield %
				found	calc.	
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{COOCH}_2\text{CH}_2\text{OCH}_2\text{P(OC}_2\text{H}_5)_2 \end{array}$	123—123.5 (0,5)	1,4380	1,1496	57,93	58,00	70
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{COOCH}_2\text{CH}_2\text{OCH}_2\text{P(OC}_2\text{H}_5)_2 \\ \\ \text{OC}_2\text{H}_5 \end{array}$	124—125 (0,5)	1,4470	1,1274	56,28	56,45	70
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{P(OC}_2\text{H}_5)_2 \\ \\ \text{OC}_2\text{H}_5 \end{array}$	126—128 (0,5)	1,4490	1,0683	59,26	59,25	35
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{P(OC}_2\text{H}_5)_2 \end{array}$	117—118 (0,5)	1,4400	1,0897	61,47	60,97	52
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{P(OC}_2\text{H}_5)_2 \\ \\ \text{OC}_2\text{H}_5 \end{array}$	171—172 (0,5)	1,4490	1,1240	81,00	80,74	10
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$						

The constants of the phosphonic and phosphinic esters are given in Table 1, and the products of their cyclization are given in Table 2.

TABLE 2

Formula	B. p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR		Yield %
				found	calc.	
$\begin{array}{c} \text{O}-\text{CH}_2-\text{P}=\text{O} \\ \quad \quad \\ \text{CH}_2-\text{CH}_2-\text{O} \quad \text{OC}_2\text{H}_5 \end{array}$	97—97,5 (0,5)	1,4336	1,2538	35,56	35,83	60
$\begin{array}{c} \text{O}-\text{CH}_2-\text{P}=\text{O} \\ \quad \quad \\ \text{CH}_2-\text{CH}_2-\text{O} \quad \text{C}_2\text{H}_5 \end{array}$	115—116 (1)	1,4750	1,2317	33,96	34,28	82
$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{P}=\text{O} \\ \quad \quad \\ \text{CH}_2-\text{CH}_2-\text{O} \quad \text{C}_2\text{H}_5 \end{array}$	87—88 (0,5)	1,4730	1,1214	36,93	37,03	62
$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{P}=\text{O} \\ \quad \quad \\ \text{CH}_2-\text{CH}_2-\text{O} \quad \text{OC}_2\text{H}_5 \end{array}$	88—90 (0,5)	1,4588	1,1614	38,58	38,59	40

Experimental

Synthesis of Diethyl 2-Acetoxyethoxymethylphosphonate. The reaction was carried out in a three-necked flask fitted with stirrer, reflux condenser, thermometer, and dropping funnel. 2-Acetoxyethyl chloromethyl ether [9] was gradually added dropwise to triethyl phosphite at 150°. The rate of addition was regulated by the rate of liberation of ethyl chloride. Two fractionations from an Arbuzov flask gave diethyl 2-acetoxyethoxymethylphosphonate in 70% yield. B.p. 123° (0.5 mm); d_4^{20} 1.1496; n_D^{20} 1.4380; calculated MR 57.93; found MR 58.00. $\text{C}_9\text{H}_{19}\text{O}_6\text{P}$. Calculated: P 12.30%; Found: P 12.17; 12.17%.

Synthesis of Ethyl (2-Acetoxyethoxymethyl)ethylphosphinate. 2-Acetoxyethyl chloromethyl ether (19.5 g) was added to diethyl ethylphosphonite (19.3 g), which was heated to 142° in a three-necked flask fitted with reflux condenser, thermometer, and dropping funnel, at such a rate that we could observe the uniform burning of the ethyl chloride liberated in the reaction. The product of this reaction was twice distilled from an Arbuzov flask. B.p. 124–125° (0.5 mm); d_4^{20} 1.1274; n_D^{20} 1.4470; calculated MR 56.28; found MR 56.45. $\text{C}_9\text{H}_{19}\text{O}_5\text{P}$. Calculated: P 13.02%; Found: P 12.83; 12.89%. The yield of ethyl (2-acetoxyethoxymethyl)ethylphosphinate was 22.5 g (70%).

Synthesis of Ethyl (4-Acetoxybutyl)ethylphosphinate. The reaction between diethyl ethylphosphonite and 4-bromobutyl acetate was carried out directly in the Arbuzov flask with the object of distilling off the ethyl bromide formed while the reaction proceeded. The 4-bromobutyl acetate was prepared from tetrahydrofuran and acetyl bromide. Acetyl bromide was added dropwise to tetrahydrofuran at 90° (with reflux of the tetrahydrofuran). Vacuum fractionation of the reaction products gave 4-bromobutyl acetate, b.p. 88–90° (10 mm), in 87% yield; n_D^{20} 1.4600; d_4^{20} 1.3678.

The bromo ester was added dropwise to 8.8 g of ethylphosphonous ester heated to 130°. Fractionation gave 7.5 g (54%) of a product of b.p. 126–128° (0.5 mm). Refractionation gave 4.8 g (35%) of pure ethyl (4-acetoxybutyl)ethylphosphinate; b.p. 127° (0.5 mm); d_4^{20} 1.0683; n_D^{20} 1.4490; calculated MR 59.26; found MR 59.25; $\text{C}_{10}\text{H}_{21}\text{O}_5\text{P}$. Calculated: P 13.14%; Found P 13.27; 13.12%.

Synthesis of Diethyl 4-Acetoxybutylphosphonate. The reaction between triethyl phosphite and 4-bromobutyl acetate was analogous to the preceding reaction. 4-Bromobutyl acetate (70 g) was added dropwise to 60 g of triethyl phosphite heated to 130°. Fractionation gave diethyl 4-acetoxybutylphosphonate, b.p. 117–118° (0.5 mm), in 52% yield; d_4^{20} 1.4400; n_D^{20} 1.0897; calculated MR 61.47; found MR 60.97. $\text{C}_{10}\text{H}_{21}\text{O}_5\text{P}$. Calculated: P 12.30%; Found: P 12.44; 12.47%.

In addition we isolated a higher fraction, b.p. 171-172° (0.5 mm), in 10% yield. Its constants and the results of analysis showed that this product was 4-acetoxybutyl ethyl 4-acetoxybutylphosphonate; n_D^{20} 1.4490; d_4^{20} 1.1240; calculated MR 81.00; found MR 80.74. $C_{24}H_{40}O_7P$. Calculated: P 9.18%; Found: P 9.56; 9.63%.

Synthesis of 2-Ethoxy-1,4,2-dioxaphosphorinane 2-Oxide. A mixture of 24 g of diethyl 2-acetoxyethoxymethylphosphonate with 0.5 ml of phosphoric acid as catalyst was heated in an Arbuzov flask to 175-180° for ten hours; cyclization then occurred with elimination of ethyl acetate. The ethyl acetate was distilled off as it was formed, and almost the theoretical amount was collected. Three vacuum fractionations gave a pure product; b.p. 97° (0.5 mm); yield 60%; n_D^{20} 1.4536; d_4^{20} 1.2538; calculated MR 35.56; found MR 35.83. $C_5H_{11}O_4P$. Calculated: P 18.66%; Found: P 18.81; 18.62%. 2-Ethoxy-1,4,2-dioxaphosphorinane 2-oxide is readily soluble in water and organic solvents.

Synthesis of 2-Ethyl-1,4,2-dioxaphosphorinane 2-Oxide. The procedure was as for the preceding reaction: a mixture of 19.2 g of ethyl (2-acetoxyethoxymethyl)ethylphosphinate and 0.5 ml of phosphoric acid was heated for nine hours at 180°. We obtained an 82% yield of ethyl acetate. Fractionation gave a product of b.p. 116° (1 mm) in 82% yield; d_4^{20} 1.2317; n_D^{20} 1.4750; calculated MR 33.96; found MR 34.28. $C_5H_{11}O_3P$. Calculated: P 20.66%; Found: P 20.45; 20.64%.

Synthesis of 2-Ethyl-1-1,2-oxaphosphorinane 2-Oxide. For reaction by the same procedure we took 13.5 g of ethyl (4-acetoxybutyl)ethylphosphinate and 1 ml of phosphoric acid. Ethyl acetate was distilled off and collected in 80% yield. Vacuum fractionation gave a product of b.p. 87-88° (0.5 mm) in 62% yield; d_4^{20} 1.1211; n_D^{20} 1.4730; calculated MR 36.93; found MR 37.03. $C_2H_5O_2P$. Calculated: P 20.94%; Found: P 20.42%.

Synthesis of 2-Ethoxy-1,2-oxaphosphorinane 2-Oxide. For reaction by the same procedure we took 64 g of diethyl 4-acetoxybutylphosphonate and 2 ml of phosphoric acid. Vacuum fractionation gave 16.4 g (40%) of a product of b.p. 88-90° (0.5 mm); d_4^{20} 1.1614; n_D^{20} 1.4588; calculated MR 38.58; found MR 38.59. $C_6H_{13}O_3P$. Calculated: P 18.90%; Found: P 18.79; 18.75%.

Summary

1. By the action of 4-bromobutyl acetate and of 2-acetoxyethyl chloromethyl ether on triethyl phosphite and on diethyl ethylphosphonite the corresponding phosphonic and phosphinic esters were synthesized.

2. These latter substance, when heated in presence of phosphoric acid, reacted with elimination of ethyl acetate and gave derivatives of 1,2-oxaphosphorinane and 1,4,2-dioxaphosphorinane 2-oxides.

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β -KETO PHOSPHONIC AND PHOSPHINIC ESTERS

COMMUNICATION 6. PRODUCTS OF THE REACTION OF CHLORO- AND BROMO-ACETONE WITH DIETHYL ETHYLPHOSPHONITE AND WITH SODIUM ETHYL ETHYLPHOSPHONITE

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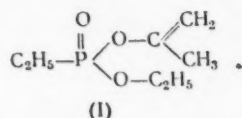
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1772-1778, October, 1960

Original article submitted May 16, 1959

It was shown in previous investigations [1] that the reaction of α -halo carbonyl compounds with triethyl phosphite and with sodium diethyl phosphite proceeds in a complex fashion. Together with the normal reaction products, β -keto phosphonic esters, unsaturated phosphoric esters and, in the case of sodium diethyl phosphite, epoxy phosphonic esters are obtained. The course of the reaction is greatly affected by the nature of the halogen (Cl, Br), by the substituents in the α -halo ketones [1], and by the reaction conditions.

The present paper reports the results of a study of analogous reactions with diethyl ethylphosphonite and with sodium ethyl ethylphosphonite having the purpose of determining the effect of replacing the ethoxyl of triethyl phosphite or sodium diethyl phosphite by ethyl directly linked to phosphorus.

In the reaction of chloroacetone with diethyl ethylphosphonite [2] we obtained a high yield of a product having: b.p. 56-57° (0.5mm); d_4^{20} 1.0351; n_D^{20} 1.4329; MR found 44.68, $C_7H_{13}O_3PF$. Calculated MR 44.98. On transesterification with ethanol the product gave acetone and diethyl ethylphosphonate [3]; b.p. 93-95° (22 mm); d_4^{20} 1.0223; n_D^{20} 1.4120. Titration with peroxyphthalic acid gave an unsaturation of 100%, reckoned on one double bond. All these results indicate that the product was ethyl isopropenyl ethylphosphonate (I):



The Raman spectrum of ethyl isopropenyl ethylphosphonate (I) contained the following frequencies (cm^{-1}):

300 (2d*), 330 (2d), 410 (1d), 449 (0), 490 (2b*), 534 (2), 683 (6b), 743 (2), 780 (2), 103 (2), 859 (1), 900 (1), 947 (1), 985 (4), 1033 (4b), 1101 (4), 1163 (1), 1235 (2d), 2262 (2), 1292 (2), 1370 (3), 1400 (4), 1448 (3), 1461 (4b), 1475 (0), 1660 (5b), 8728 (1b), 2776 (1), 2801 (1), 2870 (1b), 2884 (3), 2924 (6b), 2942 (4b), 2982 (4), 3003 (3d), 3034 (2).

The ultraviolet absorption spectrum of ethyl isopropenyl ethylphosphonate (I) is shown in Fig. 1. In methanol solution the absorption followed a smooth curve (Curve 1) with a slight maximum in the region of wavelengths less than 2400 Å, and it did not change appreciably in methanol containing sodium methoxide (Curve 2). The absence in the Raman spectrum of the valence-vibration frequency of the $\text{C}=\text{O}$ group ($1710\text{-}1715\text{ cm}^{-1}$) and the

*d = diffuse; b = broad.

presence of the frequency 1660 cm^{-1} corresponding to the valence vibration of the $\text{C}=\text{C}$ group, and also the absence of the maximum characteristic of the absorption of the keto group in the ultraviolet spectrum, confirm the structure of the product as ethyl isopropenyl ethylphosphonate (I).

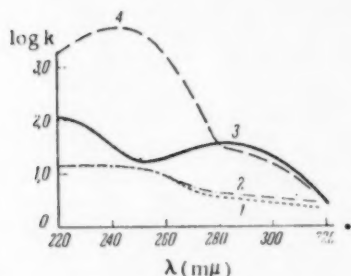
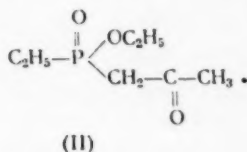


Fig. 1. Ultraviolet absorption spectra: 1) Ethyl isopropenyl ethylphosphonate in CH_3OH ; 2) the same in $\text{CH}_3\text{OH} + \text{CH}_3\text{ONa}$; 3) product of b.p. $89-90^\circ$ (0.5 mm) in CH_3OH ; 4) the same in $\text{CH}_3\text{OH} + \text{CH}_3\text{ONa}$.

A somewhat different picture was obtained in the reaction of diethyl ethylphosphonite with bromoacetone. As in the case of the reaction between triethyl phosphite and bromoacetone [4], at first two products were isolated. The first had the following constants: b.p. $53-55^\circ$ (0.5 mm); d_4^{20} 1.0309; n_D^{20} 1.4305; MR found 44.7; these are close to those of the above-described product of the reaction of diethyl ethylphosphonite with chloroacetone. The Raman spectrum of the product was completely identical with that of the product (I) obtained from chloroacetone, which confirms that ethyl isopropenylethylphosphonate is obtained also in the reaction with bromoacetone. The second product had: b.p. $89-90^\circ$ (0.5 mm); d_4^{20} 1.1436; n_D^{20} 1.4543.

On analogy with the product of the reaction of bromoacetone with triethyl phosphite [4], it may be expected that in the reaction of bromoacetone with diethyl ethylphosphonite the formation may occur of ethyl acetonyl ethylphosphonate (II):

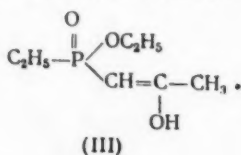


As would be expected for a compound of structure (II), the transesterification reaction did not go with the product of b.p. $89-90^\circ$ (0.5 mm). However, some of the data obtained for the compound of b.p. $89-90^\circ$ (0.5 mm) were not in accord with the formula (II). Thus, we did not succeed in preparing a crystalline 2,4-dinitrophenylhydrazone, and titration with peroxyphthalic acid gave an unsaturation of about 7%. Elementary analysis gave a phosphorus content which was 1% less than that calculated for the structure (II). The molecular refraction (42.17) differed considerably from that calculated for the structure (II) (44.28). Hence, chemical data did not give a clear picture of the structure of the high-boiling product. Supplementary information on the structure was obtained by a study of the spectra. We determined the Raman spectrum and the ultraviolet absorption spectrum. The ultraviolet spectrum of the product of b.p. $89-90^\circ$ is given in Fig. 1. The absorption curves of the product in isooctane and methanol solutions (Curve 3) coincided completely and had an absorption maximum at 2800 Å , characteristic for ketones, a minimum at 2500 Å , and a maximum in the region below 2200 Å . When dissolved in methanol containing sodium methoxide, the product showed strong absorption in the region of 2400 Å , which indicated a considerable concentration of enolate ions in an alkaline medium (Curve 4). We observed a similar picture in the case of acetonylphosphonic ester and its homologs [5].

The Raman spectrum of the product of b.p. $89-90^\circ$ (0.5 mm) contained the following frequencies (cm^{-1}):

273 (1d), 321 (1), 392 (1d), 442 (0), 460 (1d), 518 (2), 574 (3), 612 (0), 670 (5), 690 (2), 780 (1), 810 (2), 850 (1), 936 (0), 979 (2), 1040 (3b), 1100 (3), 1121 (2), 1215 (3), 1236 (2d), 1290 (3b), 1404 (3), 1446 (3b), 1461 (4), 1598 (0), 1657 (4), 1710 (4), 2734 (1b), 2870 (3b), 2886 (5), 2918 (6b), 2942 (4b), 2976 (5b), 3001 (3b), 3073 (1).

Examination of the Raman spectrum showed the presence of the frequency $1710(4)\text{ cm}^{-1}$, indicating the presence of a keto group, and the frequency $1657(4)\text{ cm}^{-1}$, which is characteristic for the $\text{C}=\text{C}$ double bond. The presence of the frequency $1657(4)\text{ cm}^{-1}$ in the spectrum may be explained by some ethyl isopropenylethylphosphonate (I) impurity or the enolization of ethyl acetonyl ethylphosphonate ($\text{II} \rightleftharpoons \text{III}$).



Purification of the product of b.p. 89-90° (0.5 mm) by distillation through a column of 17-plate efficiency did not lead to any change in constants. Neither did the Raman spectrum change, and the intensity of the frequency 1657 cm^{-1} retained its previous value. A difference in the character of the absorption was noteworthy; the band at 1660 cm^{-1} in the spectrum of ethyl isopropenyl ethylphosphonate was somewhat broader than that at 1657 cm^{-1} in the spectrum of the product (I) of b.p. 89-90° (0.5 mm). Hence, the possibility of any ethyl isopropenyl ethylphosphonate impurity (which has a considerably lower boiling point) is excluded.

By further investigations we succeeded in determining the cause of the difference of the chemical and physical properties of the fraction of b.p. 89-90° (0.5 mm) from those corresponding to the structure (II). Analysis showed that the fraction of b.p. 89-90° (0.5 mm) contained 8.3% of bromine, which indicated that the fraction contained impurities that were not separated by distillation through an efficient column. The resolution of the fraction of b.p. 89-90° (0.5 mm) was carried out chromatographically on silica gel*. We isolated two substances: The first had b.p. 72-74° (1 mm), n_D^{20} 1.4738, and d_4^{20} 1.3748; it contained bromine. In analysis and molecular refraction it corresponded to the empirical formula $C_7H_{14}O_3PBrF$; MR found 52.55; calculated MR 52.74.

The second substance b.p. 75-78° (1 mm); n_D^{20} 1.4502; d_4^{20} 1.0833 corresponded in analysis and molecular refraction to ethyl acetonylphosphinate (II).

The Raman spectrum of ethyl acetonyl ethylphosphinate (II), b.p. 75-78° (1 mm), contained the following frequencies (cm^{-1}):

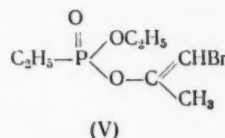
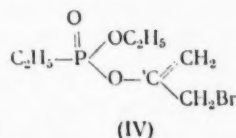
277 (2), 323 (2), 378 (2d), 392 (1), 441 (2d) 459 (2), 518 (3), 576 (5), 616 (1), 670 (7b), 691 (0), 717 (1), 782 (2), 811 (4b), 850 (2), 980 (2), 1039 (3), 1101 (4), 1125 (3), 1211 (4), 1232 (2d), 1290 (2), 1402 (3b), 1458 (5b), 1657(0), 1710 (4), 2884 (2d), 2919 (6b), 2948 (4d), 2976 (5b), 3001 (2).

The spectrum of the product of b.p. 72-74° (1 mm) contained the following frequencies (cm⁻¹):

279 (0), 327 (0), 357 (1d), 442 (0), 489 (1), 516 (1), 557 (2), 573 (1), 672 (3b), 743 (0), 793 (2), 810 (1b), 983 (2), 1039 (b), 1102 (2), 1153 (1), 1235 (1), 1286 (1b), 1384 (2), 1446 (3), 1462 (3), 1657 (6), 2870 (1), 2887 (2b), 2923 (5b), 2945 (2d): 2979 (3b), 3074 (2b).

Examination of these spectra and their comparison with the spectrum of the product of b.p. 89-90° (0.5 mm) showed that the latter consisted of a superposition of the spectra of the substances separated by chromatography and, for example, contained the carbonyl frequency (1710 cm^{-1}) of ethyl acetonylethylphosphinate and the frequencies of 1657 and 3073 cm^{-1} characteristic of the presence of a C=C bond in the product of b.p. 72-74° (1 mm).

On the basis of the above chemical and spectroscopic data, the product of b.p. 72-74° (1 mm) may be assigned one of the following formulas:



The formation of the products (IV) and (V) could be explained by the presence of 1,1- and 1,3-dibromoacetones in the original bromoacetone. However, the great difference between the boiling points of mono- and di-bromoacetones and the large amount of the fractions corresponding to (IV) and (V) makes it improbable that such a large amount of dibromoacetone impurity would be present in the original monobromoacetone. It must therefore be considered that the structure of the product of b.p. 72-74° (1 mm), and also the way in which it is formed, has not been elucidated and requires further investigation. It is interesting that Jacobson, Griffin, Preis, and Jensen [6], in the reaction of triethyl phosphite with iodoacetone, obtained not only diethyl acetonylphosphonate, but also the ester formed by the enol form of diethyl acetonylphosphonate with diethyl hydrogen phosphate, which has an analogy with the formation of the bromine-containing product (IV) or (V). The American

*The spectrum was taken with a short exposure because of the strong background.

authors did not isolate the intermediate halogen-containing compound; they considered that the mechanism of this interesting reaction was obscure.

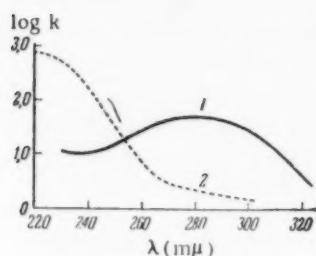
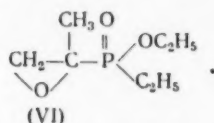


Fig. 2. Ultraviolet absorption spectra: 1) Ethyl acetonyl ethylphosphinate in CH_3OH ; 2) product of b.p. 72-74° (1 mm) in CH_3OH .

acetonyl ethylphosphinate (II). The product was not transesterified by ethanol, being recovered unchanged, and it did not give a dinitrophenylhydrazone. Titration with peroxyphthalic acid showed the absence of unsaturation.

These data and the analogy with the reaction between chloro- and bromo-acetones and sodium diethyl phosphite, which leads to the formation of diethyl 1, 2-epoxy-1-methylethylphosphonate [1], permits us to conclude that the product isolated was ethyl (1,2-epoxy-1-methylethyl)ethylphosphinate (VI):

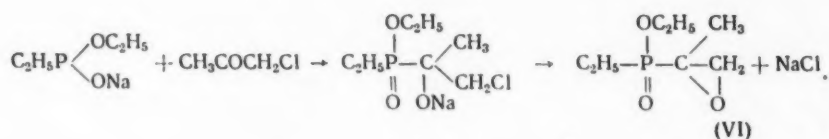


The Raman spectrum of the product (VI) contained the following frequencies (cm^{-1}):

230 (1), 285 (4b), 323 (4), 348 (1b), 466 (2), 525 (1), 582 (5), 513 (4), 709 (3b), 728 (1), 786 (3b), 844 (4), 923 (3), 988 (2b), 1039 (2), 1068 (1), 1098 (3), 1150 (0), 1160 (0), 1201 (3), 1226 (2), 1246 (2), 1286 (0), 1324 (7), 1383 (1), 1409 (2), 1446 (2), 1463 (4), 1660 (0**), 2729 (3b), 2773 (2), 2810 (1), 2869 (2), 2886 (4), 2932 (5b), 2983 (4b), 3066 (2b).

The spectrum confirmed that the product was an epoxy compound. The frequencies of the keto group and the $\text{C}=\text{C}$ bond were absent. The presence of an epoxide ring was indicated by the frequency of 3066 cm^{-1} , which corresponds to CH valence vibrations at an α -epoxide ring [8].

The ultraviolet spectrum of ethyl (1, 2-epoxy-1-methylethyl) ethylphosphinate (VI) in methanolic solution is shown in Fig. 3 (Curve 1). The smoothness of the absorption curve (1) of the product and the change in the absorption in presence of sodium methoxide (Curve 2) without the appearance of a maximum corresponding to the keto group are reminiscent of the spectrum and its corresponding changes for the case of diethyl 1,2-epoxy-1-methylethylphosphonate [5]. Hence, in the case of sodium ethyl ethylphosphonite reaction proceeds as in the case of sodium diethyl phosphite with formation of an epoxy ester [1].



*An increment of + 0.62 was assumed for the epoxide ring.

**Corresponds to traces of an unsaturated compound.

The material given in this paper shows that the reactions between diethyl ethylphosphonite or sodium ethyl ethylphosphonite, on the one hand, and chloroacetone or bromoacetone, on the other, take the same courses as in the case of triethyl phosphite and sodium diethyl phosphite.

Experimental

Raman spectra were determined with an ISP-51 three-prism spectrograph; the mercury lines 4358 Å and 4047 Å were used as exciting radiation. Ultraviolet absorption spectra were determined with an SF-4 quartz spectrophotometer.

Action of Diethyl Ethylphosphonite on Chloroacetone. In an atmosphere of carbon dioxide 20.1 g of chloroacetone was introduced into a four-necked flask fitted with thermometer, dropping funnel, tube for the entry of carbon dioxide, and tube for the removal of ethyl chloride, and dropwise addition was made of 32.5 g of diethyl ethylphosphonite [2]. The addition of diethyl ethylphosphonite was regulated so that the temperature inside the flask was 100-105°. Toward the end of the reaction the flask was heated to 105-110° for 30 min. By distillation of the reaction product through a Widmer column we isolated a product having: b.p. 56-57° (0.5 mm); d_4^{20} 1.0351; n_D^{20} 1.4329; found MR 44.68; calculated MR 44.98. Found: P 17.51%, $C_7H_{15}O_3PF$. Calculated: 17.41%.

The yield was 27.3 g (61.46%). The substance had a pleasant odor.

On transesterification of the product (5 g) with ethanol (10 ml) in presence of sodium ethoxide we obtained diethyl ethylphosphonate (2.3 g), b.p. 93-95° (22 mm); d_4^{20} 1.0223 and n_D^{20} 1.4120, and acetone (2,4-dinitrophenylhydrazone), m.p. 124-125°.

Action of Diethyl Ethylphosphonite on Bromoacetone. The reaction was carried out under the conditions described for chloroacetone. For reaction we took 28 g of bromoacetone. After fractionation through a Widmer column we isolated the following fractions: The first, which amounted to 6.4 g (18%), had b.p. 53-55° (0.5 mm); d_4^{20} 1.0309; n_D^{20} 1.4305; found MR 44.70; calculated MR 44.98. Found: P 17.52%, $C_7H_{15}O_3P$. Calculated P 17.41%. Meyer titration [9] gave an unsaturation of 79.9%.

The second product, which amounted to 21.1 g (59.1%), had b.p. 89-90° (0.5 mm); d_4^{20} 1.1436; n_D^{20} 1.4543; found MR 42.17; calculated MR 44.28. Found: P 16.40; 16.22; Br 8.3%, $C_7H_{15}O_3P$. Calculated: P 17.41%. Meyer titration [9] gave an unsaturation of 3.2%. After distillation through a column of 17-plate efficiency the constants were unchanged. In a repeat experiment we isolated a product having the constants: b.p. 84-86° (0.5 mm); d_4^{20} 1.1665; n_D^{20} 1.4565. Found: P 15.73; Br 10.48%.

The resolution of the fraction of b.p. 89-90° (0.5 mm) was effected by chromatography on silica gel. For 10 g of the fraction we took 150 g of ASK silica gel, which had been treated with hydrochloric acid, washed free from chloride ions, and dried. Ether and methanol were used as eluants. By elution with ether we obtained 2.0 g of a product having the following properties: b.p. 72-74° (1 mm); d_4^{20} 1.3748; n_D^{20} 1.4738; found MR 52.55, $C_7H_{14}O_3PBrF$. Calculated MR 52.74. Found: P 11.92; Br 30.93%, $C_7H_{14}O_3PBr$. Calculated: P 12.06; Br 31.12%.

After elution with methanol we isolated 4.2 g of a product having the following properties: b.p. 75-78° (1 mm); d_4^{20} 1.0833; n_D^{20} 1.4502; found MR 44.18; calculated MR 44.28. Found: P 17.21; Br 0.2%, $C_7H_{15}O_3P$. Calculated: P 17.41%.

Action of Sodium Ethyl Ethylphosphonite on Chloroacetone. The reaction was carried out in a three-necked flask fitted with stirrer, dropping funnel, and reflux condenser. From 4.3 g of sodium (excess) and 20.2 g of ethyl hydrogen ethylphosphonite in 150 ml of ether we prepared the sodium derivative [7]. The resulting solution of the sodium derivative was added dropwise with stirring to an ethereal solution of 15.3 g of chloroacetone. When the addition was complete, the mixture was heated for 90 min in a water bath. The precipitate of sodium chloride was centrifuged away, ether was distilled off, and the residue was fractionated through a Widmer column. We isolated 10.2 g (34.6%) of product having the following properties: b.p. 81.5-82° (1 mm); d_4^{20} 1.0914; n_D^{20} 1.4505, found MR 43.92; calculated MR 44.23. Found: P 17.57%, $C_7H_{15}O_3P$. Calculated: P 17.41%. In transesterification experiments with ethanol the product was recovered unchanged.

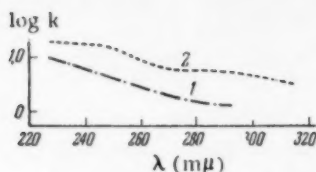


Fig. 3. Ultraviolet absorption spectra: 1) Ethyl (1,2-epoxy-1-methylethyl) ethylphosphinate in CH_3OH ; 2) the same in $\text{CH}_3\text{OH} + \text{CH}_3\text{ONa}$.

Summary

1. The action of diethyl ethylphosphonite on chloroacetone results in the formation of ethyl isopropenyl ethylphosphonate. In the case of bromoacetone, as well as ethyl isopropenyl ethylphosphonate, ethyl acetonylethylphosphinate is formed.

2. The reaction of chloroacetone with sodium ethyl ethylphosphonite gives ethyl (1,2-epoxy-1-methylethyl) ethylphosphinate.

3. A study was made of the Raman spectra and ultraviolet absorption spectra of previously undescribed compounds.

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FURFURYL ESTERS OF SOME ACIDS OF TERVALENT ARSENIC

Gil'm Kamai and N. A. Chadaeva

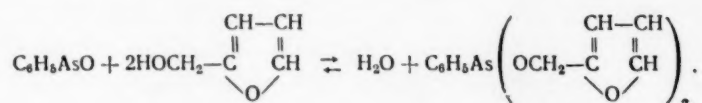
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1779-1782, October, 1960

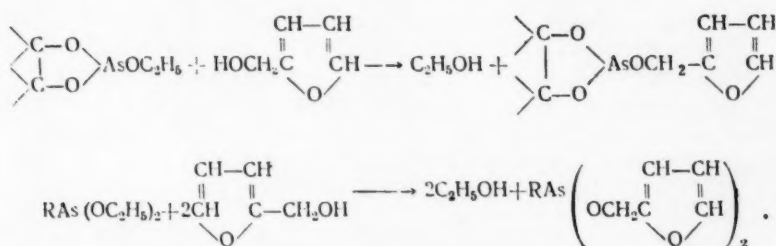
Original article submitted May 15, 1959

Furfuryl derivatives of arsenic have received little study [1, 2]. No furfuryl esters of acids of arsenic have been described in the literature. The present work forms the further development of our investigations [3] on various esters of acids of trivalent arsenic.

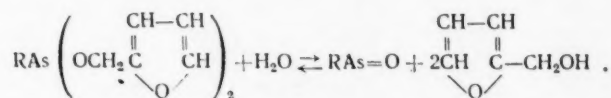
For the synthesis of arsonous acids we used the following three methods. In the reaction between furfuryl alcohol and arsenic trichloride in presence of bases in a dry ether medium we were unable to isolate trifurfuryl arsenite in a pure state because of the resinification of the reaction products. When furfuryl alcohol was heated with arsenosobenzene, a good yield was obtained of difurfuryl benzenearsonite:



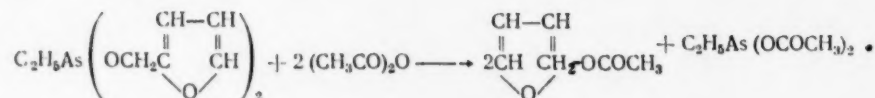
However, when arsenious oxide was heated with furfuryl alcohol in a vacuum, no trifurfuryl arsenite could be isolated. The transesterification method gave the best results. The furfuryl esters of arsenious and arsonous acids were obtained when ethyl esters of these acids were heated with furfuryl alcohol:



With the exception of furfuryl o-phenylene arsenite, the furfuryl esters that we isolated were colorless oils; they turned yellow in the light, and acquired a brown color when allowed to stand for a long time. In their properties the furfuryl esters were reminiscent of the corresponding alkyl esters of trivalent arsenic acids. They were rapidly hydrolyzed by water with liberation of arsenious oxide or the corresponding arsenoso compound and furfuryl alcohol:



Difurfuryl ethane arsonite reacted with acetic anhydride with formation of furfuryl acetate and a mixed anhydride:



We studied also the tendency of the esters synthesized to undergo polymerization and copolymerization. Our experiments showed that, when heated with benzoyl peroxide, furfuryl esters of arsonous acids are resinified. When mixtures containing 20% of the furfuryl ester of an arsonous acid, 79% of methyl methacrylate, and 1% of benzoyl peroxide were heated, solid copolymers were obtained.

Experimental

Trifurfuryl Arsenite. A mixture of 16.1 g of triethyl arsonite and 22.5 g of furfuryl alcohol was heated at the boil for two hours in a distilling flask having a Vigreux column. Distillation gave the following fractions: Fraction I, b.p. 78-80° (760 mm), 7.4 g; Fraction II, b.p. 146-165° (5 mm) and n_D^{20} 1.5103, 2.1 g; Fraction III, b.p. 165-193° (4-2 mm) and n_D^{20} 1.5397, 23.0 g. Fraction III was redistilled. We then isolated 10.7 g of a fraction of b.p. 191.5-192° (3 mm). Found: As 21.04, 21.01%. $\text{C}_{15}\text{H}_{15}\text{O}_6\text{As}$. Calculated: As 21.03%.

Trifurfuryl arsonite is a slightly yellowish clear thick oil. It is hydrolyzed by water, and is readily soluble in many organic solvents; n_D^{20} 1.5432; d_4^{20} 1.4127; found MR 79.49; calculated $\text{AR}_D\text{As} \dots 9.94$. An attempt to prepare trifurfuryl arsonite by heating a mixture of 10 g of arsenious oxide with 30 g of furfuryl alcohol was not successful. The mixture was converted into a dark-brown mass, which decomposed when distilled at a residual pressure of about 2 mm.

Difurfuryl Ethane arsonite. A mixture of 22.3 g of diethyl ethane arsonite and 22.0 g of furfuryl alcohol was heated in an oil bath in a stream of carbon dioxide. The contents of the flask began to boil at a bath temperature of 125°. Heating was continued for two hours, and the mixture was then distilled. The main fraction (24.3 g) had b.p. 135-136° (2.5 mm). Found: As 24.98; 24.91%. $\text{C}_{12}\text{H}_{15}\text{O}_4\text{As}$. Calculated: As 25.12%. The difurfuryl ethane arsonite isolated was a thick pale-yellow liquid; n_D^{20} 1.5307; d_4^{20} 1.3409; found MR 68.75; calculated $\text{AR}_D\text{As} \dots 9.75$. On long standing in the light it darkened in color; it was hydrolyzed by water.

Difurfuryl Benzene arsonite. A mixture of 8.4 g of arsenosobenzene and 10.0 g of furfuryl alcohol was heated in an Arbuzov distilling flask at a residual pressure of 11-12 mm at 70-75° for two hours. Vacuum distillation followed, and gave: Fraction I, b.p. 70-72° (12 mm), 2.9 g; Fraction II, b.p. 184-188° (3 mm) and n_D^{20} 1.5747, 10.3 g. On redistillation of Fraction II we isolated a substance of b.p. 179.5-181° (2 mm). Found: As 21.68; 21.63%. $\text{C}_{16}\text{H}_{15}\text{O}_4\text{As}$. Calculated: As 21.64%. The substance isolated was, therefore, pure difurfuryl benzene arsonite. The ester is a thick yellow liquid; n_D^{20} 1.5785; d_4^{20} 1.3719; found MR 83.98; calculated $\text{AR}_D\text{As} \dots 10.09$. It is hydrolyzed by water with the liberation of arsenosobenzene.

Ethylene Furfuryl Arsenite. A mixture of 9.5 g of ethyl ethylene arsonite and 5.5 g of furfuryl alcohol was heated to 140° in a stream of carbon dioxide. Ethanol (b.p. 77-78° and n_D^{20} 1.3635) began to distill off. Vacuum fractionation of the residue gave 6.5 g of a fraction of b.p. 90-91° (2 mm). Found: As 32.18; 32.30%. $\text{C}_7\text{H}_9\text{O}_4\text{As}$. Calculated: As 32.28%. Ethylene furfuryl arsonite is a clear liquid; d_4^{20} 1.5871; n_D^{20} 1.5340; found MR 45.45; calculated $\text{AR}_D\text{As} \dots 8.58$. When allowed to stand in the air it rapidly darkens in color and becomes brown. It is hydrolyzed by water with formation of arsenious oxide. It is readily soluble in many anhydrous organic solvents.

(Chloromethyl) ethylene Furfuryl Arsenite. A mixture of 12.6 g of (chloromethyl)ethylene ethyl arsonite and 6 g of furfuryl alcohol was heated to 140° in a distilling flask for four hours. This was followed by distillation, and we isolated the following fractions: Fraction I, 1.3 g of ethanol, b.p. 77-78.5° and n_D^{20} 1.3626; Fraction II, 9.3 g (50.2%), b.p. 128-130° (2 mm). Found: As 26.81%. $\text{C}_8\text{H}_{10}\text{O}_4\text{ClAs}$. Calculated: As 26.70%. The ester isolated was an oily liquid which rapidly became yellow in the light; it was hydrolyzed by water with formation of a white precipitate; n_D^{20} 1.5398; d_4^{20} 1.6039; found MR 54.87; calculated $\text{AR}_D\text{As} \dots 8.52$.

Furfuryl o-Phenylene Arsenite. A mixture of 10.1 g of ethyl o-phenylene arsenite and 4.5 g of furfuryl alcohol was heated, given suitable treatment, and fractionated with collection of ethanol and a fraction of b.p. 150-153° (2 mm) and m.p. 46-49°. When allowed to stand in the light, the crystals darkened in color. Found: 26.73; 26.41%. $C_{11}H_9O_4As$. Calculated: As 26.74%. Furfuryl o-phenylene arsenite is readily soluble in benzene, carbon tetrachloride, chloroform, ether, and methyl methacrylate; it is hydrolyzed by water.

Reaction of Difurfuryl Ethane arsonite with Acetic Anhydride. A mixture of 7.8 g of difurfuryl ethane arsonite and 4.8 g of acetic anhydride was heated in a distilling flask to 170° for three hours. On the next day the reaction mixture was vacuum-fractionated. We collected the following fractions: Fraction I, b.p. 46-100° (11 mm) and n_D^{20} 1.4585, 7.1 g; Fraction II, b.p. 100-127° (10 mm) and n_D^{20} 1.4720, 3.8 g. The first fraction was washed with sodium carbonate solution and then twice with water. After being dried over anhydrous sodium sulfate the liquid was distilled; b.p. 176-177°, n_D^{18} 1.4616. For furfuryl acetate the literature gives: b.p. 175-177° (464 mm) and n_D^{15} 1.4603. From the second fraction we isolated a substance of b.p. 126-127° (10 mm) and n_D^{20} 1.4693, which is in accord with the literature for $C_2H_5As(OCOCH_3)_2$ [4].

Hydrolysis of Trifurfuryl Arsenite. A mixture of 1.6 g of trifurfuryl arsenite and 30 ml of water was refluxed in a round-bottomed flask for one hour. The precipitate formed was found to be arsenious oxide. Found: As 75.51%. As_2O_3 . Calculated: As 75.43%.

Hydrolysis of Difurfuryl Benzenearsonite. A mixture of 1.2 g of difurfuryl benzenearsonite and 25 ml of water was boiled for one hour. The precipitate that separated when the mixture was cool was found to be arsenosobenzene, m.p. 130-132°.

Data on the copolymerization of furfuryl esters of trivalent-arsenic acids with methyl methacrylate are given in the table.

TABLE

No.	Substances	Comp. %	Start of copolymerization	End of copolymerization
1	$C_2H_5As\left(OCH_2-\text{furfuryl}\right)_2$	20	After 24 hr. at 80°	After 480 hr. at 150°
	Methyl methacrylate Benzoyl peroxide	79 1		Clear, dark-yellow resin
2	$C_6H_5As\left(OCH_2-\text{furfuryl}\right)_2$	20	After 20 hr at 100°	After 48-51 hr at 150°
	Methyl methacrylate Benzoyl peroxide	79 1		Clear, yellow, solid resin
3	$\begin{array}{c} CH_2-O \\ \quad \diagup \\ CH_2-O \end{array} As-OCH_2-\text{furfuryl}$	20	After 24 hr at 80°	After 18-20 hr at 100° Clear, colorless, solid resin
	Methyl methacrylate Benzoyl peroxide	79 1		
4	$\begin{array}{c} CH_2-O \\ \quad \diagup \\ CH-O \end{array} As-OCH_2-\text{furfuryl}$ CH_2Cl	20	After 24 hr. at 80°	After 20 hr at 100° Clear, yellowish, solid resin
	Methyl methacrylate Benzoyl peroxide	79 1		
5	$\left(\text{furfuryl}-CH_2O\right)_2As$	20	After 6 hr at 100-120°	After 36 hr at 150° Dark-brown resin
	Methyl methacrylate Benzoyl peroxide	79 1		

Summary

1. By the transesterification of lower alkyl esters of acids of trivalent arsenic, furfuryl esters of arsonous and arsenious acids were synthesized for the first time and their properties were studied.

2. On being heated with methyl methacrylate in presence of benzoyl peroxide, the furfuryl esters of trivalent arsenic acids formed clear gel-like and solid copolymers.

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REACTION OF N₂O₄ WITH ORGANIC COMPOUNDS

COMMUNICATION 4. CONVERSION OF THE NITROMETHYL GROUP INTO THE TRINITOMETHYL GROUP

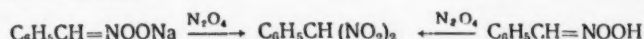
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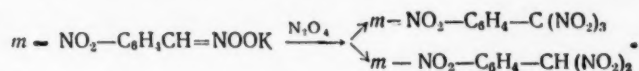
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1783-1786, October, 1960

Original article submitted May 27, 1959

In a previous communication [1] we described the reaction of N₂O₄ with aci- α -nitrotoluene and its salt with formation of α, α -dinitrotoluene:

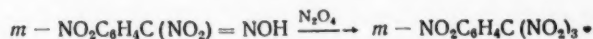


We decided to extend this reaction to compounds of this series having substituents in the nucleus: salts of m, α - and p, α -dinitrotoluenes. The experiments showed that for the reaction of N₂O₄ with the potassium salt of m, α -dinitrotoluene in the required direction the process must be carried out in dichloroethane at 70° with a large amount of N₂O₄ (21 moles of N₂O₄ per mole of the salt). In this case, in addition to m, α, α -trinitrotoluene (17.5%) there is formed $m, \alpha, \alpha, \alpha$ -tetranitrotoluene (14.5%), so that the entry of two nitro groups into the nitromethyl group occurs:



We suppose that the entry of two nitro groups into the nitromethyl group proceeds via some intermediate product. Such a product could be m -nitrobenzonitrolic acid, which was found in the reaction mixture when the reaction was carried out without the application of heat. This compound contains an oxime group, and the formation of an α, α, α -trinitrotoluene is to be expected from it on analogy with the formation of α, α -dinitrotoluenes from aromatic aldoximes [2].

Our experiments in fact showed that, on treatment with excess of N₂O₄ (in dichloroethane at 50-60°), m -nitrobenzonitrolic acid reacts smoothly and gives $m, \alpha, \alpha, \alpha$ -tetranitrotoluene in good yield (86%):



This gives us grounds to affirm that aromatic nitrolic acids form an intermediate stage in the formation of α, α, α -trinitrotoluenes from salts of α -mononitrotoluenes under the action of N₂O₄. On the basis of this conclusion we were able to find reaction conditions such that the yield of α, α, α -trinitrotoluenes from salts of α -mononitrotoluenes was considerably increased. The essence of the method lay in the addition of N₂O₄ in two portions: the first portion was added under conditions ensuring maximum yield of the nitrolic acid, and the second portion was added under optimum conditions for the conversion of the nitrolic acid into the α, α, α -trinitrotoluene. By this method we obtained $m, \alpha, \alpha, \alpha$ -tetranitrotoluene and the previously undescribed $p, \alpha, \alpha, \alpha$ -tetranitrotoluene in yields of 58-60%. Under the action of alcoholic alkali the second of these was converted into the previously unknown p, α, α -trinitrotoluene.

The conversion of the nitromethyl group into the trinitromethyl group can be regarded also as occurring through the intermediate formation of a dinitromethyl group. It is known that in presence of N_2O_4 a salt of α,α -dinitrotoluene is converted into α,α,α -trinitrotoluene [3]. In the present work we found that a salt of m,α,α -trinitrotoluene similarly gives m,α,α,α -tetranitrotoluene. However, the intermediate formation of the aci-form of the α,α -dinitrotoluene in the formation of the α,α,α -trinitrotoluene was not detected, and in their normal forms α,α -dinitrotoluenes do not react with N_2O_4 .

Experimental

m,α - and p,α -Dinitrotoluenes were prepared by the nitration of α -nitrotoluene [4]. α -Nitrotoluene was prepared by the nitration of toluene with oxides of nitrogen [5]. The potassium salts of m,α - and p,α -dinitrotoluenes and m,α,α -trinitrotoluene were prepared in yields of more than 90% by treatment of hot alcoholic potassium ethoxide. m,α,α -Trinitrotoluene was prepared by the nitration of α,α -dinitrotoluene [6], which was obtained by the action of N_2O_4 on benzaldomine [3].

Reaction of N_2O_4 with the Potassium Salt of m,α -Dinitrotoluene. Experiment with application of heat. To a suspension of 1 g of the potassium salt of m,α -dinitrotoluene in 20 ml of dry dichloroethane heated to 70° , 9 g of N_2O_4 (26 moles per mole of the salt) was added in one portion. The reaction was accompanied by vigorous effervescence, and the temperature fell rapidly to 40° and then rose to 65° . The reaction mixture was filtered from inorganic salt, washed with water, and extracted with two 20 ml portions of 10% sodium bicarbonate solution. From the bicarbonate extracts α,α -trinitrotoluene was isolated by precipitation with 10% sulfuric acid after the addition of 1 g of urea. The precipitate of m,α,α -trinitrotoluene was filtered off, washed with water, and dried in the air at room temperature. Yield 0.18 g (17.5%). After reprecipitation from dichloroethane with petroleum ether m,α,α -trinitrotoluene had m.p. $127-129^\circ$, undepressed by admixture of known m,α,α -trinitrotoluene. The literature [6] gives m.p. $128-130^\circ$.

On evaporation of the dichloroethane solution remaining after the extraction of m,α,α -trinitrotoluene, 0.18 g (14.5%) of m,α,α,α -tetranitrotoluene was obtained. After crystallization from alcohol m,α,α,α -tetranitrotoluene had m.p. $63-64^\circ$, undepressed by admixture of known m,α,α,α -tetranitrotoluene. The literature [2] gives m.p. 65° .

Experiment without application of heat. To a suspension of 1 g of the potassium salt of m,α -dinitrotoluene in 30 ml of dry ether at 3° we added 1.1 g of N_2O_4 (2.5 moles per mole of the salt) in one portion. The temperature of the reaction mixture rose rapidly to 15° , and there was simultaneous feeble effervescence. The reaction mixture was filtered from inorganic salt and evaporated at room temperature. A residue of 0.7 g (67%) of crystals of m -nitrobenzonitrolic acid remained.

After being reprecipitated twice from dichloroethane with heptane, m -nitrobenzonitrolic acid formed colorless crystals, m.p. $69-71^\circ$ (decomp.), readily soluble in ether, less readily in dichloroethane, and poorly soluble in petroleum ether and heptane. m -Nitrobenzonitrolic acid is readily soluble in aqueous solutions of caustic alkalis and alkali-metal bicarbonates. However, unlike m,α,α -trinitrotoluene, m -nitrobenzonitrolic acid in sodium carbonate solution begins to decompose within a few minutes with separation of an organic precipitate. This decomposition can be hastened by the application of heat. In solutions of potassium and sodium hydroxides m -nitrobenzonitrolic acid is more stable; by the rapid acidification of these solutions unchanged nitrolic acid can be isolated, but after one day in these solutions the substance undergoes profound change. It is no longer possible to separate m -nitrobenzonitrolic acid from these solutions by acidification.

A confirmatory synthesis of m -nitrobenzonitrolic acid was carried out by the method described by Wieland and Semper [7] for the preparation of benzonitrolic acid (acidification of an aqueous solution of the potassium salt of m,α -dinitrotoluene and potassium nitrite with oxalic acid). The m -nitrobenzonitrolic acid, which was obtained in 84% yield, was reprecipitated from dichloroethane with heptane and then had m.p. $69-71^\circ$ (decomp.), undepressed by admixture of a sample of the m -nitrobenzonitrolic acid obtained by the reaction of N_2O_4 with the potassium salt of m,α -dinitrotoluene. The substance dissolved in 10% potassium hydroxide with a reddish-orange coloration. Analysis showed that the m -nitrobenzonitrolic acid contained one molecule of water of crystallization. Found: C 36.70; 36.80; H 3.19; 3.23; N 18.36; 18.56%. $C_7H_5N_3O_5 \cdot H_2O$. Calculated: C 36.69; H 3.08; N 18.34%.

m -Nitrobenzonitrolic acid has been described previously by other authors. According to the analytical data (for nitrogen) cited, it did not contain water of crystallization, and it melted at 82° [9] or 89° [8]. On attempting to obtain such an acid by the methods of these authors (action of N_2O_4 [8] of fuming nitric acid [9] or

on the oxime), we invariably obtained the above-described crystal hydrate, m.p. 69-71°. However, like the anhydrous nitrolic acid described in the literature, the substance that we obtained gave a good yield of 3,4-bis-m-nitrophenylfuroxan (m.p. 185°) with benzene at the boil and gave the benzoyl derivative (m.p. 145°) under the action of benzoyl chloride in presence of caustic alkali.

Analysis of 3,4-Bis-m-nitrophenylfuroxan. Found: C 50.88; 50.97; H 2.54; 2.72; N 16.89; 17.16%. $C_{14}H_8N_4O_6$. Calculated: C 51.22; H 2.46; N 17.07%. The literature [8] gives m.p. 185°.

Analysis of O-Benzoyl-m-nitrobenzonitrolic Acid. Found: C 53.50; 53.47; H 3.03; N 13.47; 13.34%. $C_{14}H_9N_3O_6$. Calculated: C 53.34; H 2.88; N 13.33%. The literature [8] gives m.p. 145°.

The structure of the m-nitrobenzonitrolic acid that we obtained was confirmed also by a spectroscopic method; this will be reported in a future publication.

Reaction of N_2O_4 with the Potassium Salt of m, α , α -Trinitrotoluene. To a suspension of 3 g of the potassium salt of m, α , α -trinitrotoluene in 15 ml of dry carbon tetrachloride heated to 70° we added 5.3 g (5 moles per mole of the salt) of N_2O_4 in one portion. The course of the reaction and the treatment of the mixture was similar to those described above for the reaction of N_2O_4 with the potassium salt of m, α -dinitrotoluene (experiment with application of heat). We obtained 1.4 g (46%) of m, α , α -tetranitrotoluene. After crystallization from alcohol the substance had m.p. 63-64°, undepressed by admixture of known m, α , α -tetranitrotoluene.

Reaction of N_2O_4 with m-Nitrobenzonitrolic Acid. N_2O_4 (4.5g) was added to a solution of 1 g of m-nitrobenzonitrolic acid in 20 ml of dichloroethane; (m.p. 69-73° with decomp.) after which the reaction mixture was heated rapidly to 60-70°. The mixture was washed with water and several times with sodium bicarbonate solution; it was evaporated at room temperature. A residue of 1 g (84%) of crystals of m, α , α -tetranitrotoluene remained. After crystallization from alcohol the substance had m.p. 63-64°, undepressed by admixture of known m, α , α -tetranitrotoluene.

Procedure in the One-stage Synthesis of α , α , α -Trinitrotoluenes from Salts of α -Nitrotoluenes. N_2O_4 (2.8g) was added to a suspension of 1 g of the potassium salt of the α -nitrotoluene in 20 ml of dry ether cooled to 0°. The cooling bath was removed, and a solution of 6 g of N_2O_4 in 20 ml of dry dichloroethane was added to the reaction mixture, the temperature of which then rapidly rose to 50° (most of the ether and the excess of oxides of nitrogen then boiled off). The reaction mixture was filtered from mineral salt, washed twice with water and twice with 10% sodium bicarbonate solution, and evaporated in an open crystallization dish at room temperature. The residual oil was added in small portions to concentrated sulfuric acid (slight rise in temperature), and the mixture was shaken in a separating funnel; the substance then crystallized out. The α , α , α -trinitrotoluene was filtered off, washed with water, and dried in air at room temperature.

By this method α , α , α -trinitrotoluenes were prepared from the potassium salt of m, α -dinitrotoluene (60% yield of m, α , α -tetranitrotoluene) and the potassium salt of p, α -dinitrotoluene (58 % yield of p, α , α -tetranitrotoluene).

p, α , α -Tetranitrotoluene is a colorless crystalline substance of m.p. 46-47° (from hexane), readily soluble in the cold in alcohol, ether, chloroform, and dichloroethane, and somewhat less soluble in hexane and petroleum ether. Found: C 31.00; 30.79; H 1.59; 1.53; N 20.46; 20.70%. $C_7H_4N_4O_8$. Calculated: C 30.89; H 1.48; N 20.59%.

Like m, α , α -tetranitrotoluene [2], when heated with alcoholic potassium hydroxide our p, α , α -tetranitrotoluene passed into the potassium salt of p, α , α -trinitrotoluene, which on acidification gave p, α , α -trinitrotoluene itself, a colorless crystalline substance of m.p. 72-73° (from methanol), readily soluble in aqueous solutions of caustic alkalis and alkali-metal bicarbonates. Found: C 37.22; 37.17; H 2.48; 2.60; N 8.54; 18.45%. $C_7H_5N_3O_6$. Calculated: C 37.01; H 2.22; N 18.50%. The potassium salt of p, α , α -trinitrotoluene differs from the sodium salt in being poorly soluble in water. The salts are yellow.

Summary

1. When heated with salts of α -nitrotoluenes, N_2O_4 reacts with formation of α , α , α -trinitrotoluenes.
2. The entry of two nitro groups into the side chain of an α -nitrotoluene, which was observed for the first time, proceeds with intermediate formation of the nitrolic acid.

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TAUTOMERISM OF NITRO COMPOUNDS

COMMUNICATION 2. POLAROGRAPHIC INVESTIGATION OF THE KINETICS OF THE TAUTOMERIC TRANSFORMATIONS OF α -NITROTOLUENE

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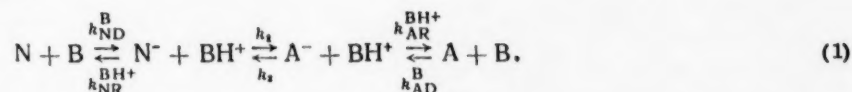
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1787-1795, October, 1960

Original article submitted March 24, 1959; additions made June 8, 1960

In the preceding communication [1] it was stated that the kinetics of the transformations in the system α -nitrotoluene \rightleftharpoons its anions \rightleftharpoons its aci form had been investigated polarographically. We now describe the procedure used in this work and give the results of the experiments.

Experimental

An investigation was made of the polarographic behavior of the aci and nitro forms of α -nitrotoluene; it was found that these forms differed in behavior*. This fact made it possible for us to study the kinetics of transformations in the system



In this equation the constants have the same significance as in the preceding communication; N and A denote the nitro and aci forms of α -nitrotoluene; B and BH^+ denote the base and its conjugate acid. The kinetics of the transformation of aci- α -nitrotoluene into the nitro form were studied in the pH range 1-4, of the nitro form into the anion in the pH range 7-10, and of the anion into the nitro form in the pH range 4-6. Also, the dissociation constants of the aci and nitro forms were determined polarographically and potentiometrically.

The kinetics of the reactions were studied in buffer solutions, so that the measured reaction rate was the over-all rate of reaction with all the bases present in the buffer mixture. To find the rate constants for reaction with each of the bases we measured reaction rates at different concentrations of the given base, keeping the pH of the solution, the concentrations of the other bases, and the ionic strength constant. Thus, we determined the rate of reaction of α -nitrotoluene with OH^- , HPO_4^{2-} , and $H_2BO_3^-$ and the rate of reaction of aci- α -nitrotoluene with H_2O , CH_3COO^- , $ClCH_2COO^-$ and the nitrate ion. As will be shown below, the rate of reaction of α -nitrotoluene with water is very low; its value ($< 5 \cdot 10^{-5} \text{ sec}^{-1}$) lies within the limits of experimental error and so cannot be determined experimentally. As Maron and La Mer [2] showed, the reaction under consideration obeys the Bronsted equation. To find, and to determine with greater accuracy, the constants of the Bronsted equation, we determined also the rate of reaction of α -nitrotoluene with NH_3 and with acetate and diethylbarbiturate ions.

*The anions of the substances are polarographically inactive.

The work was carried out with a manual polarograph. Current measurement was carried out with an M-91 microammeter. The potential of the dropping electrode with respect to the anode (a saturated calomel electrode) was determined in the kinetic measurements with an LM-1 voltmeter accurately within 0.01 v. In the taking of polarograms the potential of the dropping electrode was determined potentiometrically with respect to a subsidiary saturated calomel electrode with a P-4 potentiometer with an extended measurement range [3]. The experiments were carried out in a thermostated cell [4] at $25 \pm 0.1^\circ$. The cathode was a dropping mercury electrode fitted with a blade for forced drop removal [5]. Most of the work was carried out with a capillary having the following characteristics: $m = 1.81$ mg/sec; $t = 0.29$ sec; $m^{2/3} t^{1/6} = 1.209$ $\text{mg}^{2/3} \cdot \text{sec}^{-1/2}$. Before the measurements were carried out, oxygen was removed from the solution by passage of nitrogen saturated with solvent vapor [4].

The measurements were carried out in the following buffer solutions: $\text{HCl} + \text{KCl}$; $\text{CH}_3\text{CO}_2\text{Na} + \text{HCl}$; $\text{K}_2\text{HPO}_4 + \text{C}_3\text{H}_4(\text{OH})(\text{CO}_2\text{H})_3$; $\text{K}_2\text{HPO}_4 + \text{Na}_2\text{B}_4\text{O}_7$; $\text{Na}_2\text{B}_4\text{O}_7 + \text{HCl}$; $\text{Na}_2\text{B}_4\text{O}_7 + \text{NaOH}$. The measurement of the pH values of the solutions and the direct determination of the dissociation constant of the aci form were carried out with the aid of a glass electrode and an LP-5 or LP-59 potentiometer. The reagents used had the following characteristics: 1) α -Nitrotoluene; b.p. 88° (2 mm); n_D^{20} 1.5320; 2) Potassium salt of α -nitrotoluene. Found: K 22.43; 22.11%. $\text{C}_7\text{H}_6\text{NO}_2\text{K}$. Calculated: K 22.32%. The salts for the preparation of buffer mixtures were of "Chemically Pure" or "Pure for Analysis" qualities.

Polarographic Investigation of Aci and Nitro Forms of α -Nitrotoluene. The determination of the polarograms of the nitro form of α -nitrotoluene presented no difficulties. On the other hand, because of the instability of the aci form it was not possible to determine their polarograms in the usual way; they were determined as follows. Buffer solution of pH 1.15 (9.5 ml) was poured into the cell and left to attain 25° while nitrogen was passed to remove dissolved oxygen. The dropping electrode was polarized at the given potential and the residual current was measured. After this, 0.5 ml of an aqueous-alcoholic (8% of alcohol by volume) solution of the potassium salt of α -nitrotoluene was poured rapidly into the cell and vigorously agitated with nitrogen for 5-7 sec; then, after every 15 sec, the limiting current was read off; it diminished continuously because of the conversion of the aci form into the nitro form. In these experiments the potential of the dropping electrode was varied from -0.1 to -1.2 v in 0.1-v intervals (and in 0.05- and 0.025-v intervals in the region of the rise in the curve). The value of the current corresponding to the aci form at a given potential was found by extrapolation of the values found to zero time. The concentration of the substance investigated in the cell was $4.8 \cdot 10^{-4}$ mole/liter; the alcohol concentration was 0.4%.

Figure 1 gives the polarograms of the aci form (Curves 1 and 1a) and nitro form of α -nitrotoluene (Curve 2). Curve 1a was obtained in presence of a little methyl red, added for the suppression of the polarographic maximum. The polarogram of the nitro form was determined in the same buffer solution and with the same concentration of the substance under investigation. The half-wave potentials $E_{1/2}$ of the two forms in solution at pH 1.15 were found to be -0.52 v for the nitro form and -0.66 for the aci form.

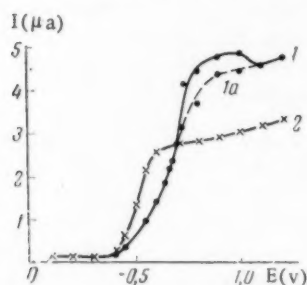


Fig. 1. Polarographic reduction waves: 1) Aci form of α -nitrotoluene; 1a) ditto in presence of methyl red; 2) α -nitrotoluene at pH 1.15.

The height of the wave of the aci form was about 1.5 times that of the nitro form. This difference is probably to be explained by the fact that reduction of the aci form occurs with the participation of six electrons, whereas in the reduction of the nitro form under the same conditions only four electrons participate.

Kinetics of the Dissociation of α -Nitrotoluene. An examination of the polarograms of α -nitrotoluene determined at various pH values showed that at pH < 5.5 α -nitrotoluene gives a clearly marked reduction wave in which the limiting current is independent of pH and is proportional to the α -nitrotoluene concentration in the solution. With rise in the pH of the solution to above 6 at a given α -nitrotoluene concentration, as a result of its dissociation, the wave height begins to fall with time and tends to a certain limit. The magnitude of this limit appears to correspond to the undissociated part of the α -nitrotoluene which is in equilibrium with its anion. With rise in pH the value of the current established diminishes and approximates to zero at pH 9.0. The equilibrium character of this limit is indicated by the fact that for a given pH of the solution the same value of the limiting current is obtained when a salt of α -nitrotoluene is taken instead of α -nitrotoluene itself. Hence, the equilibrium state can be attained both by

the dissociation of α -nitrotoluene and by the recombination of its anion. Fig. 2 shows the relation of the height at which the α -nitrotoluene wave becomes established to pH. The points correspond to values obtained from experiments with free α -nitrotoluene, and the crosses were obtained with its salts. Fig. 2 shows that pK_N is close to 6.8. Equilibrium between α -nitrotoluene and its anion is established relatively slowly. This made it possible to follow the kinetics of the ionization of α -nitrotoluene polarographically in solutions having a pH of 7 and higher.

The kinetics of the dissociation of α -nitrotoluene were investigated in the following way. The buffer solution (18.75 ml) of given pH in the range 7-10 was poured into a cell, where it was kept with passage of nitrogen until the temperature was established at 25°. A potential of $E = -1.40$ v was applied to the dropping electrode. Rapid addition of 1.25 ml of the original 0.00625 mole/liter solution of α -nitrotoluene in aqueous alcohol (8% of ethanol by volume) was made. The analytical concentration in the cell was $3.9 \cdot 10^{-4}$ mole/liter, and the alcohol content of the final solution was 0.5%. After vigorous agitation with nitrogen for 5-7 sec, measurements of limiting current were made at definite intervals, at first after every 15 sec, and then more rarely until a constant equilibrium value was established.

Figure 3 gives graphs for the time-dependence of the logarithm of the reduced (and corrected for residual current) values of limiting current in borate buffers. The ionization of α -nitrotoluene in a buffer solution is described by an equation of the first order (with respect to α -nitrotoluene), and for a pH rise of one unit the reaction

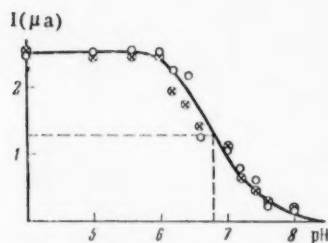


Fig. 2. Relation of the equilibrium height of the α -nitrotoluene wave to the pH of the solution.

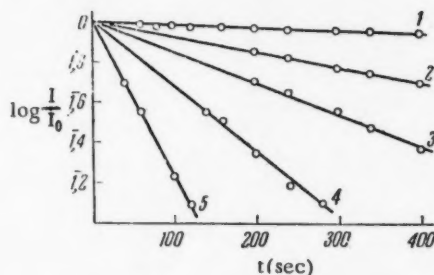


Fig. 3. Rate of dissociation of α -nitrotoluene at various pH values: 1) pH 8.00; 2) 8.68; 3) 9.00; 4) 9.50; 5) 10.00.

rates rise about tenfold. The relation of the rate constants for the ionization of α -nitrotoluene, as found from the slopes of the kinetic curves to pH at 25°, is shown in Fig. 4. It was shown by special experiments that the rate of the reaction of α -nitrotoluene with borate ions as base is very low in comparison with the rate of the same reaction with OH^- ions; this enables us to neglect the rate of dissociation of α -nitrotoluene under the action of borate ions. The second-order rate constant (for reaction with OH^-) $k_{ND}^{OH^-}$ calculated from the pH relationship was found to be 330 liters/mole·sec.

The rates of ionization of α -nitrotoluene under the action of various bases were determined as follows. A series of solutions was prepared in which the pH and ionic strength of the solution were constant, but the content of the base under study was varied. To maintain constant ionic strength of the solution (e.g., 0.2), calculated amounts of potassium chloride were added. For the calculation of rate constants, the concentrations of all solutions were recalculated as content of active base on the basis of the dissociation constant of the buffer component and the pH of the solution. The kinetic curves were determined in just the same way as in the determination of the relation of the rate of dissociation to pH. Values of the rate constants for the dissociation of α -nitrotoluene were plotted against the concentration of the base being studied. These relations were found to be represented by straight lines; in Fig. 5, by way of example, we give the straight line obtained for NH_4OH at pH 8.5. From the slopes of the lines the following values were calculated for second-order rate constants: $k_{ND}^{NH_3} = 6.7 \cdot 10^{-2}$ liter per mole · sec; $k_{ND}^{db} = 4.8 \cdot 10^{-2}$ liter/mole · sec; $k_{ND}^{HPO_4} = 5.9 \cdot 10^{-2}$ liter/mole sec; $k_{ND}^{CH_3CO_2} = 9 \cdot 10^{-4}$ liter per mole · sec; db denotes the anion of diethylbarbituric acid.

*The experiments were carried out with solutions containing also 0.02 mole/liter of potassium diethylbarbiturate in order to create the required buffering capacity.

Kinetics of the Isomerization of the Aci Form. The difference in the heights of the waves of the aci and nitro forms of α -nitrotoluene made it possible to follow the kinetics of the isomerization of the aci form. On acidification of a solution of a salt of α -nitrotoluene there is almost instantaneous formation of the aci form, which at a rate depending on the acidity of the medium passes into the nitro form. As the height of the wave of the nitro form is less than that of the aci form, isomerization is accompanied by gradual reduction of the limiting current of the polarographic wave. The kinetic curves for the isomerization were determined similarly to those for the dissociation of α -nitrotoluene. In a cell containing 19 ml of buffer solution (pH 1-4) we added 1 ml of the original 0.010 M solution of the potassium salt of α -nitrotoluene in aqueous alcohol (8% by volume). The total concentration of the substance under investigation in the cell was thus $5.0 \cdot 10^{-4}$ mole/liter, and the alcohol content was 0.4%.

The experimental values of limiting current, corrected for residual current, were recalculated as content of aci form in the solution by the formula

$$\alpha = a \frac{I_t}{I_0} - b,$$

in which α is the fraction of the aci form of α -nitrotoluene in the solution; I_t is the corrected limiting current at time t ; I_0 is the corrected limiting current extrapolated to $t = 0$. a and b are numerical coefficients calculated from the experimental values of I_0 and I_{final} . Fig. 6 gives the relation of $\log \alpha$ to t for various pH values.

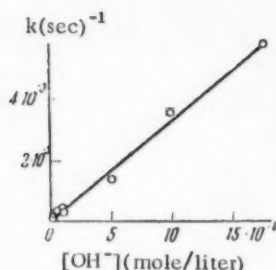


Fig. 4. Relation of dissociation rate constant for α -nitrotoluene to the concentration of hydroxyl ions in borate buffer solutions.

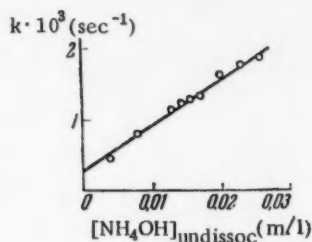


Fig. 5. Relation of dissociation rate constant for α -nitrotoluene to the concentration of undissociated NH_4OH at pH 8.5

From the slopes of the straight lines we calculated rate constants for the passage of the aci form into the nitro form. Fig. 6 shows that the rate of conversion of the aci form into the nitro form formally obeys a first-order equation over the whole pH range studied. The change in the rate constant for isomerization with rise in pH is given in Fig. 7. The relation of the rate constant to pH depends substantially on the acidity of the solution and

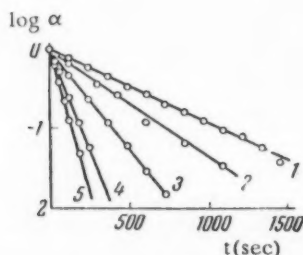


Fig. 6. Rate of isomerization of the aci form into the nitro form at various pH values: 1) pH 2.00; 2) 2.18; 3) 2.70; 4) 3.15; 5) 3.5. The analytical concentration of sodium acetate was 0.2 N; α is the fraction of aci form in the solution.

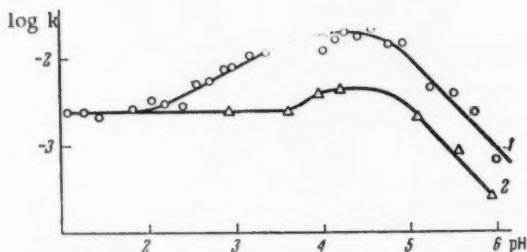


Fig. 7. Relation of rate constants for the isomerization of the aci form and the recombination of the nitro form of α -nitrotoluene in acetate buffer mixtures to the pH of the medium and the analytical concentration of sodium acetate: 1) 0.2 N $\text{CH}_3\text{CO}_2\text{Na}$; 2) 0.04 N $\text{CH}_3\text{CO}_2\text{Na}$.

the concentration of the buffer mixture. At low pH the rate of isomerization does not depend on the acidity of the solution. Then, with rise in pH the rate constant rises, and increase in the analytical concentration of salt in the buffer mixtures (e.g., of acetate in acetate buffer solutions) displaces the start of the rise in the curve in the direction of more acidic solutions. At low pH the concentration of hydroxyl ions and other bases of the buffer mixture becomes so low that the predominant effect evidently becomes the reaction of the aci form with water (as a base), which is the explanation of the constant reaction rate in a strongly acid medium. The rate constant for reaction with water calculated from the rate of isomerization at $\text{pH} < 2$ is $k_{\text{AD}}^{\text{H}_2\text{O}} = 4.14 \cdot 10^{-5}$ liter/mole-sec. As will be seen below, this value is in good accord with the Bromsted straight line for the dissociation of the aci form of α -nitrotoluene, which confirms the view advanced above.

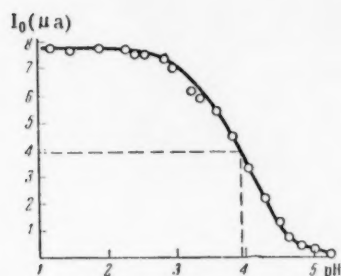


Fig. 8. Dissociation curve for aci- α -nitrotoluene.

of the aci form we found the following rate constants: $k_{\text{AD}}^{\text{cit}} = 0.28$ liter/mole-sec; $k_{\text{AD}}^{\text{CH}_3\text{CO}_2^-} = 4.5$ liters/mole-sec; $k_{\text{AD}}^{\text{ClCH}_2\text{CO}_2^-} = 8.3 \cdot 10^{-2}$ liter/mole-sec.

Kinetics of the Recombination of α -Nitrotoluene. Investigation of the isomerization of aci- α -nitrotoluene showed that at $\text{pH} \geq 2$ the initial limiting current I_0 diminishes with rise in pH because of the dissociation of the aci form. There is also a reduction in I_t with time. However, the reduction of I_t with time is observed only up to pH 4; at higher values of pH the reverse occurs: I_t begins to increase with time and tends to a certain constant value. The rise in I_t with time is to be explained by the fact that at these pH values the initial concentration (at $t = 0$) of the aci form becomes so low as a result of its dissociation that the current of the aci form becomes less than that of the nitro form formed in an extremely short time. As time passes the content of aci form diminishes to such an extent that the growth of the current corresponds completely to the kinetics of the formation of the nitro form from the anion. This circumstance enabled us to find rate constants for the formation of the nitro form at various pH values. In the pH range 4-6 kinetic curves were determined in acetate buffer mixtures by the method already described.

All the kinetic calculations were carried out on the basis of the analytical concentration of α -nitrotoluene anions in the solution, the fraction of which is $1 - (I_t/I_{\text{final}})$. Graphs for the relation of $\log [1 - (I_t/I_{\text{final}})]$ to t at various pH values are straight lines (Fig. 9). At pH values near 4 (4.15, 4.25) there is still a fair amount of the aci form at the start of the experiment, and the limiting current of this is superimposed on the limiting current of the nitro form formed. Hence, the initial parts of the kinetic curves were taken into account in these experiments (when the content of aci form exceeded 3% of the analytical concentration of the substance), and for the remaining part of the curve we took not $\log [1 - (I_t/I_{\text{final}})]$ in the calculations, but $\log [1 - (I_t - I^*)/I_{\text{final}} - I^*)]$, in which I^* corresponded to the limiting current at time t^* , when the content of aci form in the solution corresponded to 3% or less. In its turn, t^* was calculated from rate constants for the dissociation of the aci form found by the extrapolation of values for acid solutions to the given pH. The value of t^* was found to be 15 sec for pH 4.15 and 12 sec for pH 4.25; as already stated, for higher values of pH the kinetic curves were taken into account from $t = 0$ without any corrections for the content of aci form.

In Fig. 7 we give also the relation of rate constants for the formation of α -nitrotoluene to pH in two series of buffer solutions with analytical acetate concentrations of 0.2 M and 0.04 M. In solutions close to the neutral point (pH range 5-6) the rate constant increases approximately tenfold for a diminution in the pH of the medium by unity. Under these conditions the rate of the process corresponds to the recombination of the α -nitrotoluene anion. At pH 4-5 simultaneous dissociation of the aci form and recombination of the nitro form is observed.

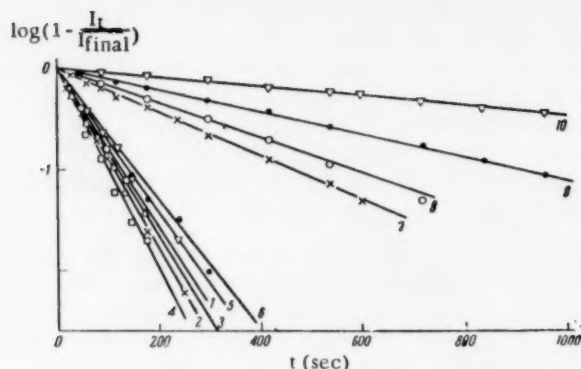


Fig. 9. Rate of formation of the nitro form at various pH values (analytical acetate concentration 0.2 N): 1) 4.15; 2) 4.25; 3) 4.40; 4) 4.55; 5) 4.75; 6) 4.90; 7) 5.25; 8) 5.50; 9) 5.75; 10) 6.00

Application of the Bronsted Equation. The rate constants found for the reaction of aci- α -nitrotoluene with various bases permitted us to evaluate the values of the rate constants of the corresponding reverse reactions. The experimentally found and the calculated values of reaction-rate constants are given in Table 1. This table gives also the dissociation constants of K_i of acids conjugate to the bases studied, the statistical factors q and p , and also the data for the plotting of curves derived from the Bronsted equation [2] (in the last three columns). The rate constants for the recombination of the aci anion with acids was found from the equation:

$$k_{AB}^{BH^+} = k_{AD}^B \frac{K_i}{K_A}$$

and the constant for the acid dissociation of the aci form was assumed to be $K_A = 1.3 \cdot 10^{-4}$.

TABLE 1

Base B	Acid BH ⁺	K_i	k_{AD}^B	$k_{AR}^{BH^+}$	p	q	$\log \frac{k_{AD}^B}{q}$	$\log \frac{k_{AR}^{BH^+}}{p}$	$\log \frac{q}{p} K_i$
H ₂ O	H ₃ O ⁺	55.5	$4.14 \cdot 10^{-3}$	17.7	1	1	-4.38	1.25	1.74
ClCH ₂ COO ⁻	ClCH ₂ COOH	$1.4 \cdot 10^{-3}$	$3.3 \cdot 10^{-2}$	0.9	1	2	-1.38	-0.05	-2.55
CH ₃ COOH	CH ₃ COOH								
HO-C-COO ⁻	HO-C-COOH	$8.7 \cdot 10^{-4}$	0.28	1.87	3	2	-0.85	-0.21	-3.24
CH ₂ COOH	CH ₂ COOH								
CH ₂ COO ⁻	CH ₂ COOH	$1.79 \cdot 10^{-6}$	4.5	0.62	1	2	0.35	-0.19	-4.45

For dissociation the Bronsted equation has the form

$$k_{AD}^B = qG_B \left(\frac{q}{p} K_i \right)^{-\beta}$$

and for recombination

$$k_{AR}^{BH^+} = pG_{BH^+} \left(\frac{q}{p} K_i \right)^{\alpha}$$

in which G_B and G_{BH^+} are constants characteristic for each substance (in the given case aci- α -nitrotoluene); α and β are coefficients, and $\alpha + \beta = 1$. Fig. 10 gives graphs constructed in accordance with the Bronsted equation. Curve 1 corresponds to the dissociation of the aci form, and Curve 2 to its recombination. From the slopes

of these straight lines and their positions we found the values: $\alpha = 0.26$; $\beta = 0.74$; $G_{BH^+} = 6.3$; $G_B = 8.0 \cdot 10^{-4}$. The ratio G_B/G_{BH^+} should be equal to K_A . Actually $G_B/G_{BH^+} = 1.27 \cdot 10^{-4}$, which practically coincides with $K_A = 1.3 \cdot 10^{-4}$.

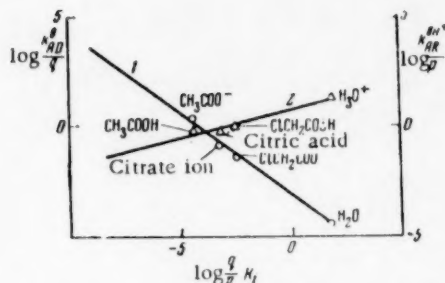


Fig. 10. Straight lines constructed in accordance with the Bronsted equation for aci- α -nitrotoluene: 1) dissociation rate constants; recombination rate constants.

The Bronsted equation was applied also to the reactions of α -nitrotoluene. Table 2 gives the experimental values of the rate constants for the dissociation and recombination of α -nitrotoluene under the influence of various bases and acids together with data for the construction of graphs in accordance with the Bronsted equation. Graphs based on these values are shown in Fig. 11.

It should be noted that several values differing somewhat from one another were obtained for k_{ND}^{OH-} . Thus, from the relation of the rate of dissociation of α -nitrotoluene to pH we found the value 330 liters/mole-sec; on the other hand, by the extrapolation of values of dissociation rate for different concentrations to zero concentration at constant pH (see e.g., Fig. 5) we found values of k_{ND}^{OH-} , which depended on the nature of the base, of 550 (borate ion), 350 (phosphate ion), 190 (diethylbarbiturate ion), and 78 (from data for NH_3) liters/mole-sec.

TABLE 2

Base B	Acid BH ⁺	K_i	k_{ND}^B	$k_{NR}^{BH^+}$	p	q	$\log \frac{k_{ND}^B}{q}$	$\log \frac{k_{NR}^{BH^+}}{p}$	$\log \frac{q}{p} K_i$
H ₂ O	H ₃ O ⁺	55,5	$8 \cdot 10^{-7}$	200	1	1	-6,40	2,3	1,75
(COO ⁻) ₂	COOH-COO	$6,4 \cdot 10^{-6}$		0,28	1	4		-0,55	-3,59
CH ₃ COO ⁻	CH ₃ COOH	$1,79 \cdot 10^{-5}$	$9 \cdot 10^{-4}$	0,13	1	2	-3,35	-0,89	-4,45
(CH ₃) ₂ CCOO ⁻	(CH ₃) ₂ CCOOH	$9,4 \cdot 10^{-6}$		0,019	1	2		-1,72	-4,73
HPO ₄ ⁼	H ₂ PO ₄ ⁻	$5,8 \cdot 10^{-8}$	$5,9 \cdot 10^{-2}$	0,089	2	3	-1,71	-1,35	-7,06
OC-N-C(OH)-C(C ₂ H ₅) ₂ -N-C-O-	Barbital	$3,7 \cdot 10^{-6}$	$4,8 \cdot 10^{-2}$		2	1	-1,32		-7,73
NH ₃	NH ₄ ⁺	$5,6 \cdot 10^{-10}$	$6,7 \cdot 10^{-2}$		1	1	-1,17		-9,25
OH ⁻	H ₂ O	$1,8 \cdot 10^{-16}$	$3,3 \cdot 10^2$		1	1	2,52		-15,75

The value of $k_{ND}^{H_2O} = 8 \cdot 10^{-7}$ liter/mole-sec given in Table 2 was found by extrapolation of the Bronsted straight line (Fig. 11) to the abscissa corresponding to the value of $\log q/pK_i$ for water, i.e., +1.8. The point corresponding to this value is shown in Fig. 11 by a cross. The straight line of the Bronsted equation (Fig. 11) was drawn through the mean value of $k_{ND}^{OH-} = 300$ liters/mole-sec; the value of $k_{NR}^{H_3O^+} = 200$ liters/mole-sec was found graphically from the kinetics of the recombination of α -nitrotoluene with acetic acid at various concentrations at pH 5.0, 5.25, and 5.5. We intend to extend the method to other tautomeric transformations.

It is the authors' pleasant duty to express their deep indebtedness to D. G. Knorre for frequent discussion of the results and valuable advice.

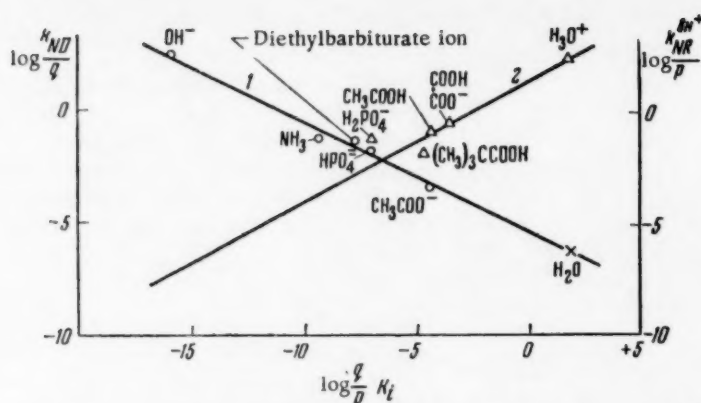


Fig. 11. Straight lines of the Bronsted equation for the nitro form of α -nitrotoluene: 1) Dissociation rate constants (X - the extrapolated value of $k^{\text{H}_2\text{O}}$); 2) recombination rate constants.

Summary

1. It was shown for the first time that the aci form of α -nitrotoluene is polarographically active.
2. A polarographic study was made of the kinetics of the dissociation of the nitro and aci forms of α -nitrotoluene under the action of various bases, and also of the kinetics of the recombination of the α -nitrotoluene anion with hydroxonium ions.
3. The dissociation constants of the aci and nitro forms of α -nitrotoluene were determined.

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STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 33. STEREOCHEMISTRY AND SOME REACTIONS OF THE ADDUCT

FORMED BY 3,4-DIHYDRO-6-METHOXY-1-VINYLNAPHTHALENE WITH MALEIC ANHYDRIDE

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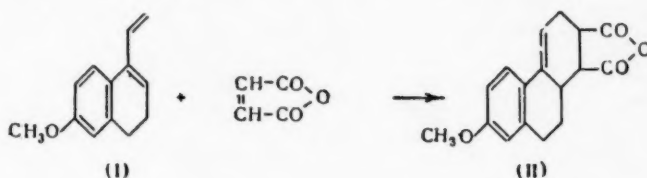
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1796-1803, October, 1960

Original article submitted May 13, 1959

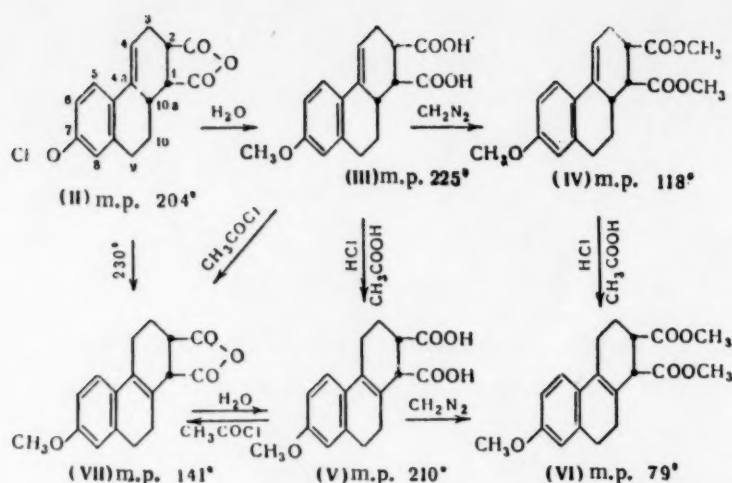
Because of difficulties in preparation 3,4-dihydro-6-methoxy-1-vinylnaphthalene (I) has received relatively little study in diene condensations, though isolated attempts have been made to utilize its adducts with maleic anhydride [1, 2], citraconic anhydride [3, 4], and mesaconic acid [2] as starting materials in the synthesis of polycyclic compounds related to steroids. Only relatively recently did this diene, as a result of the application of Normant's reaction, become fairly readily accessible, and this enabled us to make use of it in the condensation with *p*-benzoquinone for the synthesis of D-homonorsteroid compounds [5].

Continuing our investigations on the stereochemistry of cyclic dicarboxylic acids, we decided to study the stereochemistry and stereospecific transformations of the adduct formed by 3,4-dihydro-6-methoxy-1-vinylnaphthalene (I) with maleic anhydride with a view to its use in the future, both as the adduct itself (II) and as its geometric isomers, for the stereospecific synthesis of isomers of marrianolic and doisynolic acids, which are scission products of natural estrogenic hormones [6].

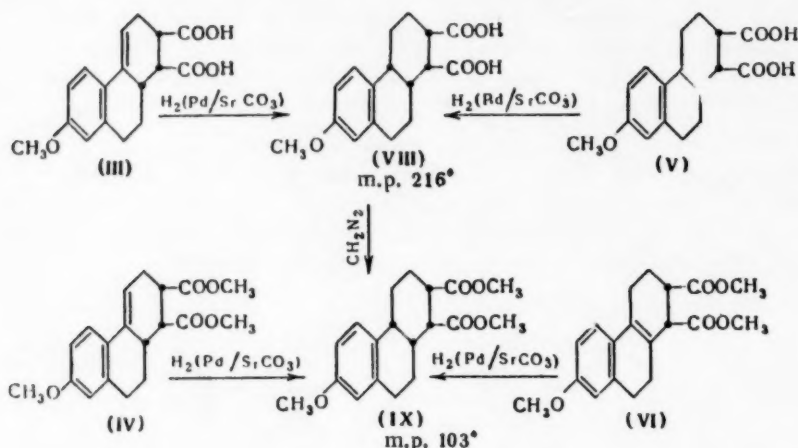


In accordance with the general laws of the diene synthesis the adduct (II), obtained in yields of up to 65% by the condensation of the diene (I) with maleic anhydride at room temperature, should have a *cis-syn* configuration and, on hydrolysis with aqueous dioxane, it gave the corresponding *cis-syn* acid (III), which was characterized as the crystalline *cis-syn* diester (IV). Unlike the previously described *cis-syn*-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acid [7], the tricyclic *cis-syn* acid (III) was found to be incapable of lactonization and, on treatment with hydrogen chloride in acetic acid, it gave the isomeric *cis*-dicarboxylic acid (V) with an inter-ring double bond, which was prepared previously by Bachmann and Controulis [2].

An analogous reaction occurs also in the case of the *cis-syn* diester (IV) and the *cis-syn* anhydride (II), which leads to the isomers (VI) and (VII), respectively. The displacement of the double bond occurs fairly readily: when the *cis-syn* anhydride (II) is heated for a short time above its melting point and when the *cis-syn* acid (III) is boiled with acetyl chloride, the *cis* anhydride (VII) is formed in good yield. The same anhydride is formed also in the condensation of the diene (I) with maleic anhydride at an elevated temperature. The structures of the compounds (V), (VI), and (VII) were proved previously by their ultraviolet spectra [2], this being the only



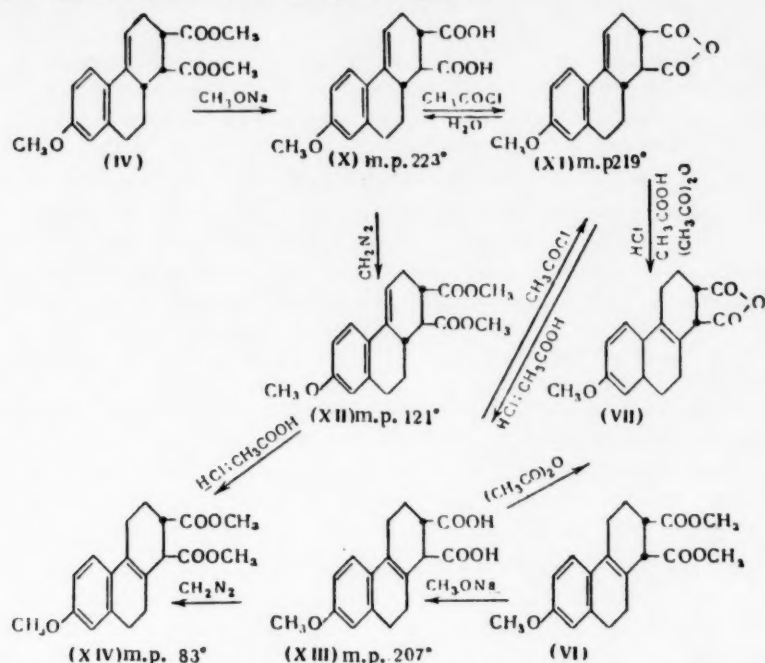
confirmation of the positions of the double bonds in them. However, the compounds (V), (VI), and (VII) which we prepared, while being identical in absorption spectrum, were found to be different in melting point from those described by Dane [1] and Bachmann [2], so that the necessity arose of a chemical proof of their structures. With this object we studied the catalytic hydrogenation of the isomeric acids (III) and (V) and of their diesters (IV) and (VI), which permitted us to confirm simultaneously the *cis-syn* configuration of the original anhydride (II).



It was found that the acid (III) is hydrogenated, though slowly, in presence of platinum oxide with formation of the individual acid (VIII), whereas the isomeric acid (V) is quite incapable of hydrogenation under these conditions. However, by use of a more active catalyst (30% of palladium on SrCO_3), which has been used previously extremely successfully for the hydrogenation of an intercycle double bond [8], the acid (V) can be hydrogenated, when a good yield is obtained of the same acid (VIII). Under the same conditions one and the same diester (IX) is formed also in the catalytic hydrogenation of the isomeric diesters (IV) and (VI). These results show quite unequivocally that the isomeric acids (III) and (V), as also their diesters, cannot be epimers with respect to C-10a and must differ only in the position of the double bond. The fact that the acid (V) and the diester (VI) are hydrogenated with great difficulty under the usual conditions proves that these compounds have an intercycle double bond, which is in accord with their ultraviolet spectra.

As shown previously [9], the catalytic hydrogenation of unsaturated cyclic 1,2-dicarboxylic acids occurs by *cis* addition from the side opposite to that of the carboxyls, in accordance with which the acid (VIII) and its diester (IX) must have a *cis-syn-cis* configuration. As the same acid and diester are formed also by the catalytic hydrogenation of the unsaturated acid (III) and its diester (IV), we may draw the well founded conclusion that the

latter have a *cis-syn* configuration, as otherwise (if they had a *cis-anti* configuration) their hydrogenation would lead to isomers with *trans* union of the rings. Hence, by a study of catalytic hydrogenation it was proved unequivocally that the compounds (V), (VI), and (VII) do indeed have an intercycle double bond, and that the original anhydride (II) formed in the diene synthesis has a *cis-syn* configuration.



A series of stereospecific transformations was studied for the case of the isomeric *cis* diesters (IV) and (VI). It was found that, on treatment with sodium methoxide and subsequent hydrolysis, the *cis-syn* diester (IV) was converted in good yield into the *trans* acid (X), which, on treatment with boiling acetyl chloride, gave the corresponding *trans* anhydride (XI) and, on treatment with diazomethane, the *trans* diester (XII). In accordance with the regularities established earlier [10], the *cis-syn* diester (IV) should have an axial methoxycarbonyl group at C₁, as a result of which the *trans* acid (X), as also its diester and anhydride obtained by its isomerization, should have a *trans-anti* configuration. Under the action of hydrogen chloride in a mixture of acetic anhydride and acetic acid, the *trans-anti* anhydride (XI) is isomerized into the above-described *cis* anhydride (VII), which has an intercycle double bond.

The *cis* diester (VI) can also be isomerized by sodium methoxide, giving after hydrolysis the only possible *trans* acid (XIII), which was characterized as its diester (XIV). The isomeric *trans* acids (X) and (XIII) differ in the position of the double bond, which was proved by the conversion of the *trans-anti* diester (XII), under the action of hydrogen chloride in acetic acid, into the *trans* diester (XIV), the structure of which was confirmed by the ultraviolet spectrum.

The *trans* acid (XIII), which has an intercycle double bond, undergoes interesting transformations. It was found that it was incapable of giving the corresponding anhydride: with boiling acetic anhydride it was converted into the *cis* anhydride (VII), and with long heating with acetyl chloride it gave the *trans-syn* anhydride (XI) as a result of a displacement of the double bond.

Experimental

Condensation of 3,4-Dihydro-6-methoxy-1-vinylnaphthalene (I) with Maleic Anhydride. Magnesium turnings (12.15 g) and a small crystal of iodine were introduced into a four-necked flask fitted with mechanical stirrer, dropping funnel, thermometer, and reflux condenser protected by a calcium chloride tube; the flask was filled with dry nitrogen, heated until the iodine began to sublime, and cooled in a stream of nitrogen. With

vigorous stirring a solution of 67.5 g of vinyl bromide in 70 ml of dry tetrahydrofuran was added at such a rate that the temperature of the mixture was kept in the range 30-35°. When the addition was complete, stirring was continued until the temperature of the mixture fell to that of the room. The reaction mixture was cooled to -20°, 100 ml of dry ether was added, and with stirring dropwise addition was made of a solution of 24.1 g of 3,4-dihydro-6-methoxy-1 (2H)-naphthalenone in 45 ml of tetrahydrofuran; the temperature of the reaction mixture was not allowed to rise above -15°. When the addition of reactants was complete, the contents of the flask were stirred further for three hours at -20°, left overnight, and finally stirred further for two hours at 30-35°. For the decomposition the contents of the flask were poured into a mixture of 300 g of ice and 65 g of ammonium chloride, which was cooled with ice and salt; the organic layer was separated, washed with sodium thiosulfate solution and water, and dried with sodium sulfate. The oil ethylenic alcohol (30 g) obtained after the distillation of solvents was divided into two portions for the subsequent dehydration.

A solution of 15 g of the unpurified ethylenic alcohol in 40 ml of dry benzene was boiled in presence of 0.1 g of N-phenyl-2-naphthylamine and an iodine crystal, with collection of the water formed in a water separator. The dehydration was practically complete in 20 min. From the reaction mixture about 20 ml of benzene was distilled off; the residue, containing the diene (I) [5], was cooled to room temperature, and a solution of 5.9 g of maleic anhydride in 40 ml of dry benzene was added. A vigorous reaction set in almost immediately, and the crystalline adduct (II) separated from the reaction mixture. From two portions of the ethylenic alcohol we obtained 22.1 g (65%, calculated on the maleic anhydride) of the adduct (II), m.p. 192-194°. After crystallization from dioxane the adduct had a constant melting point of 202-204° [1, 2]. On evaporation of the mother liquor we succeeded in isolating a little of the cis anhydride (VII), which melted at 140-141° after crystallization from a 1 : 1 mixture of acetone and ether and vacuum drying at 100°. Ultraviolet spectrum (in acetonitrile): λ_{\max} 281.5 m μ (log ϵ 4.233)*. Found: C 71.61; 71.34; H 5.33; 5.65%. $C_{17}H_{16}O_4$. Calculated: C 71.80; H 5.67%.

cis-syn Acid (III). A mixture of 0.2 g of the cis-syn anhydride (II), 2 ml of water, and 7 ml of dioxane was boiled for six hours. The solution was vacuum-evaporated to low bulk, and the crystals that separated were filtered off and dried in air. We obtained 0.18 g of the cis-syn acid (III), m.p. 220-222° (decomp.). After recrystallization from dioxane we obtained 0.12 g of pure cis-syn acid (III), m.p. 224, 225° (decomp.). Found: C 67.41; 67.42; H 6.08; 6.24%. $C_{17}H_{18}O_5$. Calculated: C 67.53; H 6.00%.

cis-syn Diester (IV). On treatment of a suspension of 0.2 g of the cis-syn acid (III) in 3 ml of methanol with ethereal diazomethane we obtained 0.18 g of the cis-syn diester (IV), m.p. 116-117°, which after crystallization from methanol had a constant melting point of 117-118° [1, 2]; ultraviolet spectrum (in alcohol): λ_{\max} 265 m μ (log ϵ 4.317); λ_{\max}^2 299.5 m μ (log ϵ 3.578).

cis Acid (V). A mixture of 1.0 g of the cis-syn acid (III) and 15 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour and then dissolved until the precipitate dissolved (15 min). Crystals were precipitated from the solution after a time and were washed with acetic acid and dried; m.p. 204-207° (decomp.) (0.55 g). After dilution of the mother liquor with 10 ml of water we obtained a further 0.2 g of substance, m.p. 204-208°. The two portions were combined and recrystallized from dioxane. We obtained 0.5 g of pure cis acid (V) with a constant melting point of 209-210° (decomp.). Found: C 67.22; 67.33; H 6.09; 6.05%. $C_{17}H_{18}O_5$. Calculated: C 67.53; H 6.00%.

cis Diester (VI). A suspension of 0.2 g of the cis acid (V) in 5 ml of methanol was treated with ethereal diazomethane. We obtained 0.18 g of the cis diester (VI), m.p. 70-73°; after crystallization from methanol and drying it had m.p. 78-79°; ultraviolet spectrum (in alcohol): λ_{\max} 276 m μ (log ϵ 4.235). Found: C 68.70; 68.75; H 6.57; 6.50%. $C_{20}H_{22}O_5$. Calculated: C 69.07; H 6.71%.

When a mixture of 1.0 g of the cis-syn diester (IV) and 5 ml of glacial acetic acid saturated with hydrogen chloride was allowed to stand at room temperature we obtained 0.90 g of the cis diester (VI), m.p. 75-76°, undepressed by admixture of the sample prepared as above.

cis Anhydride (VII). A mixture of 0.15 g of the cis acid (V) and 15 ml of acetyl chloride was boiled for three hours, acetyl chloride was vacuum-distilled off, and the crystalline residue was washed on the filter with a mixture of acetone and ether. We obtained 0.1 g of the cis anhydride (VII), m.p. 137-139°, which after crystallization from a 1 : 1 mixture of acetone and ether, had m.p. 138-139°, undepressed by admixture of a sample prepared by the diene synthesis.

* The ultraviolet spectra of the products obtained were determined in our laboratory by T. M. Fadeeva.

A mixture of 0.2 g of the cis-syn acid (III) and 30 ml of acetyl chloride was boiled for 12 hours, and we obtained 0.14 g of bright-yellow crystals. Crystallization from a 1 : 3 mixture of benzene and ether gave the cis anhydride (VII), m.p. 139-139°, undepressed by admixture of a known sample.

The cis-syn acid (III) (2.0 g) was heated in a stream of nitrogen at 220-230° for 20 min, and the colored melt was dissolved in 4 ml of boiling benzene and left to crystallize. We obtained 1.2 g of a crystalline substance, m.p. 124-125°; on evaporation of the mother liquor we isolated a further 0.3 g of the substance, m.p. 121-123°. The two portions of crystals were combined and recrystallized from a 1 : 1 mixture of acetone and ether. We obtained 0.8 g of pure cis anhydride (VII), m.p. 137-139°, undepressed by admixture of the samples prepared as above.

cis-syn-cis Diester (IX). The cis-syn diester (V) (0.60 g) was hydrogenated as a solution in 25 ml of dry dioxane over 0.1 g of 30% Pd/SrCO₃ until hydrogen ceased to be absorbed. The catalyst was filtered off, dioxane was vacuum-distilled off, and the oily residue was treated with a mixture of diethyl ether and petroleum ether, after which it crystallized out. We obtained 0.56 g of the cis-syn-cis diester (IX), m.p. 100-101°, which, after crystallization from methanol, had a constant melting point of 102-103°. Found: C 68.71; 68.51; H 7.25; 7.46%. C₁₇H₂₄O₅. Calculated: C 68.65; H 7.28%.

On hydrogenation of 0.30 g of the cis diester (VI) in a mixture of 4 ml of benzene and 4 ml of ether in presence of 0.1 g of 30% Pd/SrCO₃ we obtained 0.20 g of the cis-syn-cis diester (IX), m.p. 96-99°, which, after crystallization from methanol, had m.p. 101-102°, undepressed by admixture of the sample described above.

Cis-syn-cis Acid (VIII). The cis-syn anhydride (II) (1.0 g) was heated with a solution of sodium hydroxide (0.29 g) in water (10 ml) until dissolution was complete, the solution was filtered, and the sodium salt of the acid (III) now present was hydrogenated in presence of 30% Pd/SrCO₃ until hydrogen ceased to be absorbed. The catalyst was filtered off, and the filtrate was poured into dilute hydrochloric acid; the precipitate formed was filtered off, washed with water, and dried in air. We obtained 0.98 g of the cis-syn-cis acid (VIII), m.p. 194-200°, which, after two crystallizations from 60% aqueous dioxane, had a constant melting point of 215.5-216.5°. Found: C 67.33; 67.28; H 6.61; 6.68%. C₁₇H₂₀O₅. Calculated: C 67.09; H 6.62%.

On treatment with ethereal diazomethane, the cis-syn-cis acid (VIII) was converted in quantitative yield into the above-described cis-syn-cis diester (IX), m.p. 102-103°. Boiling of a mixture of 0.27 g of the cis-syn-cis acid (VIII) with 20 ml of acetyl chloride for three hours led to the cis-syn-cis anhydride (0.24 g), which melted at 164-165° after crystallization from benzene. Found: C 71.23; 71.26; H 6.33; 6.36%. C₁₇H₁₈O₄. Calculated: C 71.31; H 6.34%.

In the hydrogenation of 2.0 g of the cis acid (V) in 60 ml of dry dioxane in presence of 0.5 g of 30% Pd/SrCO₃ we obtained 1.72 g of the cis-syn-cis acid (VIII), m.p. 214-215.5°, undepressed by admixture of the sample prepared as above.

trans-anti Acid (X). To a solution of 2.4 g of sodium in 50 ml of dry methanol we added 1.0 g of the cis-syn diester (IV), and the mixture was boiled for 20 hours. Methanol was vacuum-distilled off to dryness, and the residue was dissolved in 200 ml of water; the solution was filtered, and to effect hydrolysis it was evaporated in a porcelain dish on a water bath. The residue of salts was filtered off, washed with a little methanol, and dissolved in 40 ml of water; the solution was filtered and acidified with hydrochloric acid. We obtained 0.80 g of the trans-anti acid (X), m.p. 218-219°, which, after crystallization from dioxane, had a constant melting point of 222-223° (decomp.). Found: C 67.28; 67.47; H 6.01; 6.09%. C₁₇H₂₀O₅. Calculated: C 67.53; H 6.00%.

trans-anti Diester (XII). On treatment of a suspension of 0.2 g of the trans-anti acid (X) in methanol with ethereal diazomethane we obtained 0.2 g of the trans-anti diester (XII), m.p. 120-121°, unchanged after recrystallization from methanol. Ultraviolet spectrum (in alcohol): λ_{\max}^1 263.5 m μ (log ϵ 4.306); λ_{\max}^2 296.5 m μ (log ϵ 3.541). Found: C 68.74; 68.80; H 6.65; 6.71%. C₁₇H₂₂O₅. Calculated: C 69.07; H 6.71%.

trans-anti Anhydride (XI). Boiling of 0.2 g of the trans-anti acid (X) with 20 ml of acetyl chloride for seven hours gave 0.13 g of the trans-anti anhydride (XI), m.p. 216-218°, which, after crystallization from benzene, had a constant melting point of 218-219°; ultraviolet spectrum (in acetonitrile): λ_{\max}^1 264 m μ (log ϵ 4.324); λ_{\max}^2 293 m μ (log ϵ 3.604). Found: C 71.92; 71.76; H 5.50; 5.63%. C₁₇H₁₆O₄. Calculated: C 71.80; H 5.67%.

Hydrolysis of 0.40 g of the trans-anti anhydride (XI) with 5% sodium hydroxide solution gave 0.38 g of the trans-anti acid (X), m.p. 210-212°, which, after crystallization from acetone, had m.p. 220-221°, undepressed by admixture of the sample prepared as above.

trans Acid (XIII). A mixture of 1.18 g of the cis diester (VI) and 50 ml of 10% sodium methoxide solution was boiled for 18 hours. Methanol was vacuum-distilled off, and the residue was dissolved in 50 ml of water; the solution was filtered and boiled with activated charcoal for four hours. The solution was filtered and carefully acidified with dilute hydrochloric acid; the precipitate formed was filtered off, washed with water, and dried in air. We obtained 0.65 g of the trans acid (XIII), m.p. 203-204°. After crystallization from 40% acetone the trans acid (XIII) had a constant melting point of 206-207°. Found: C 67.63; 67.76; H 5.92%. $C_{17}H_{18}O_5$. Calculated: C 67.53; H 6.00%.

trans Diester (XIV). On treatment of 0.1 g of the trans acid (XIII) in 5 ml of methanol with ethereal diazomethane we obtained 0.1 g of the trans diester (XIV), m.p. 76-82°, which, after crystallization from a 1 : 2 mixture of diethyl ether and petroleum ether, had m.p. 82-83°; ultraviolet spectrum (in alcohol): λ_{\max} 275.5 m μ (log ϵ 4.212). Found: C 69.12; 69.26; H 6.71; 6.73%. $C_{22}H_{22}O_5$. Calculated: C 69.07; H 6.71%.

A mixture of 0.13 g of the trans-anti diester (XII) and 1 ml of glacial acetic acid saturated with hydrogen chloride was kept at room temperature until the precipitate dissolved; acetic acid was distilled off, and a quantitative yield was obtained of the trans diester (XIV), which, after crystallization from a 1 : 1 mixture of diethyl ether and petroleum ether had m.p. 81-83°, undepressed by admixture of the sample described above.

Transformations of the trans Acid (XIII). On boiling 0.22 g of the trans acid (XIII) with 25 ml of acetyl chloride for seven hours we obtained 0.14 g of a substance of m.p. 211-214°; after crystallization from benzene it had m.p. 218.5-219°, undepressed by admixture of the trans-anti anhydride (XI) described above. On hydrolysis of 0.07 g of this anhydride with 3% sodium hydroxide solution we obtained the corresponding acid, m.p. 210-212°, which, without purification, was treated with ethereal diazomethane. After crystallization from methanol, the resulting diester had m.p. 119-120°, undepressed by admixture of the trans-anti diester (XII) and having an identical ultraviolet spectrum (in alcohol): λ_{\max}^1 263.5 m μ (log ϵ 4.257); λ_{\max}^2 297.5 m μ (log ϵ 3.609).

Boiling of 0.3 g of the trans acid (XIII) with 10 ml of acetic anhydride for eight hours gave 0.25 g of a crystalline substance of m.p. 121-123°, which, after crystallization from a 1 : 1 mixture of acetone and ether, had m.p. 138-140°, undepressed by admixture of the cis anhydride (VII).

Transformations of the trans-anti Anhydride (XI). Heating of a mixture of 0.32 g of the trans-anti anhydride (XI) and 8 ml of glacial acetic acid saturated with hydrogen chloride at 60° for seven hours gave 0.24 g of a substance which, after crystallization from a 1 : 1 mixture of benzene and acetone, had m.p. 206-207°, undepressed by admixture of the trans acid (XIII) described above.

The trans-anti anhydride (XI) (0.5 g) was added to a mixture of 4 ml of acetic anhydride and 8 ml of glacial acetic acid saturated with hydrogen chloride, and the whole was heated at 50-60° until full dissolution occurred (eight hours). Solvents were distilled off, and the crystalline residue was washed on the filter with ether. From the ethereal filtrate we isolated 0.1 g of a substance of m.p. 131-134°, which, after crystallization from benzene, had m.p. 136-138°, undepressed by admixture of the cis anhydride (VII).

Summary

1. The adduct formed by 3,4-dihydro-6-methoxy-1-vinylnaphthalene with maleic anhydride (II), and also the corresponding acid (III) and diester (IV), has a cis-syn configuration.
2. On treatment with hydrogen chloride compounds of this series are readily converted into the corresponding isomers (V), (VI), and (VII), which contain an intercycle double bond.
3. A study was made of the catalytic hydrogenation of compounds of the two isomeric series, and it was proved that the products then obtained, (VIII) and (IX), have the cis-syn-cis configuration.
4. The diesters (IV) and (VI) were isomerized under the action of sodium methoxide with formation of the corresponding isomeric trans acids (X) and (XIII), for which certain stereospecific transformations were studied.

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STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 34. TRANSFORMATIONS OF MONOESTERS OF TRICYCLIC DICARBOXYLIC ACIDS AND THE CONFORMATION OF *cis-syn*-1,2,3,9,10,10a-HEXAHYDRO-7-METHOXY-1,2-PHENANTHRENEDICARBOXYLIC ACID

V. M. Andreev, L. K. Lysanchuk, and V. F. Kucherov

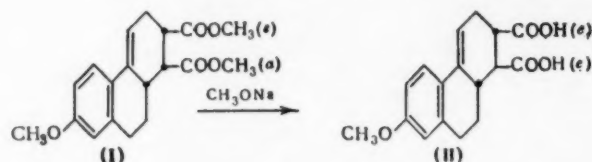
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 10, pp. 1804-1809, October, 1960

Original article submitted May 13, 1959

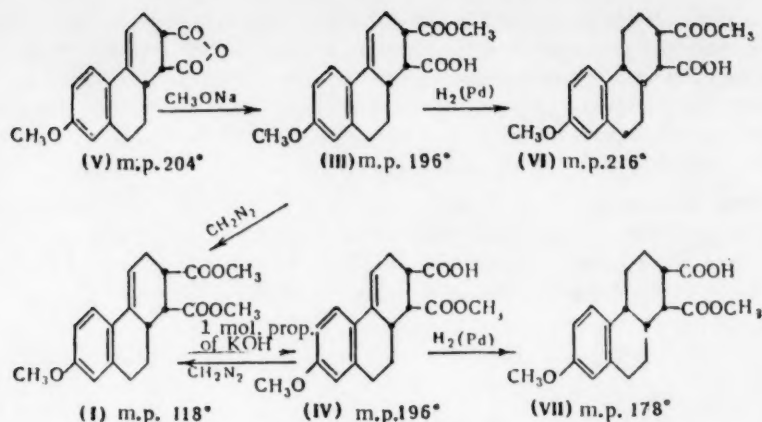
As was shown in the preceding communication [1], on isomerization with sodium methoxide the *cis-syn* diester (I) is converted into the *trans-anti* acid (II), the configuration of which was based on the view that in the original diester the methoxycarbonyl group at C₁ must be axial, so that isomerization occurs at this carboxyl.



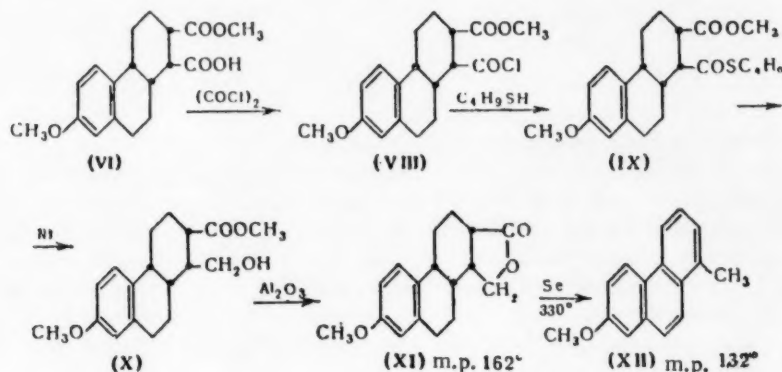
To confirm this view it was necessary to study the isomerization of the corresponding monoesters with the methoxycarbonyl group at C₁ or C₂, in which there is only one center (the methoxycarbonyl group) at which they may isomerize under the action of sodium methoxide.

For the synthesis of the corresponding *cis-syn* monoesters (III) and (IV) we applied previously described methods [2, 3], which give us grounds for supposing that the monoester (III) will be obtained by the action of sodium methoxide on the *cis-syn* anhydride (V) and the monoester (IV) by the partial hydrolysis of the *cis-syn* diester (I). It was found that these methods did in fact make it possible to prepare both of the *cis-syn* monoesters (III) and (IV), which are isomers with respect to the position of the free carboxy group and form the original *cis-syn* diester (I) on treatment with diazomethane.

However, for the unequivocal determination of the configurations of the dicarboxylic acids which could be formed by the isomerization of these monoesters it was necessary to prove the structures of the latter sufficiently rigorously. This was most conveniently done for the case of the corresponding saturated monoesters (VI) and (VII), which were formed in almost quantitative yield by the catalytic hydrogenation of the isomeric *cis-syn* monoesters (III) and (IV). As in the case of the previously described *cis-syn* acid and *cis-syn* diester [1], the catalytic hydrogenation of the isomeric *cis-syn* monoesters proceeds stereospecifically and leads to the isomeric saturated monoesters (VI) and (VII), which have the *cis-syn-cis* configuration. This was readily shown by the fact that on treatment with diazomethane they gave one and the same *cis-syn-cis* diester, as described in the preceding communication [1].

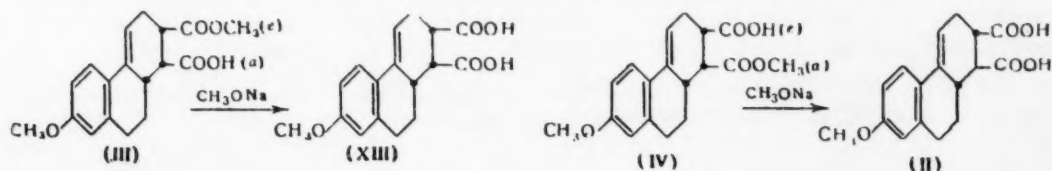


To prove the structure of one of the saturated monoesters (VI) we used the known reaction of the reduction of the free carboxy group into the corresponding primary alcohol group [4] with subsequent dehydrogenation into methoxymethylphenanthrene. In accordance with the scheme given below, the acid chloride (VIII), which was prepared from the cis-syn monoester (VI) by the action of oxalyl chloride, was converted into the thio ester (IX), which after reductive desulfurization and cyclization over alumina gave the γ -lactone (XI); the structure of the latter was confirmed by the ultraviolet spectrum. Dehydrogenation of this γ -lactone [5] by heating it with selenium led to 7-methoxy-1-methylphenanthrene (XII), m. p. 130-131°, from which we prepared 8-methyl-2-phenanthrol and its acetic ester.



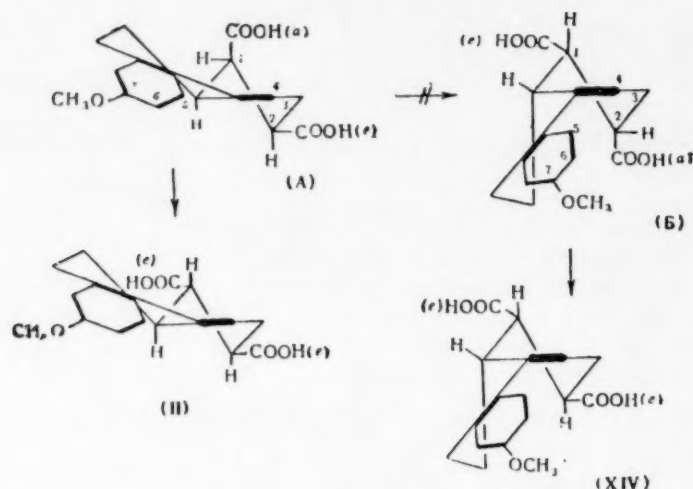
All the phenanthrene derivatives obtained had the same melting points as the corresponding derivatives of 1-methylphenanthrene [6-8], which confirms, quite unequivocally, that the original saturated cis-syn-cis monoester (VI), and therefore also the cis-syn monoester (III), has a free carboxyl at C_1 . As shown above, the second cis-syn monoester (IV) is only a structural isomer of the monoester (III) and therefore has a free carboxy group at C_2 .

The results prove that the partial hydrolysis of the cis-syn diester (I) and the addition of methanol to the cis-syn anhydride (V) proceed preferentially at the 2-carboxyl, which is clearly less effectively screened. This fact already indicates that in the cis-syn diester (I) the 2-carboxyl is equatorial and the 1-carboxyl axial; this was confirmed also by a study of the isomerization of the monoesters (III) and (IV).



It was found that the *cis-syn* monoester (III), which has a 2-methoxycarbonyl, is not isomerized by sodium methoxide and after hydrolysis gives only the original *cis-syn* acid (XIII), identical with the product described previously [1]. On the other hand, the isomeric monoester (IV) with a 1-methoxycarbonyl is readily isomerized at the boil with sodium methoxide and gives on subsequent hydrolysis the *trans-anti* acid (II), which we prepared previously [1]. This fact, which proves unequivocally the configuration of the acid (II), confirms at the same time the view that in the *cis-syn* diester (I) and the *cis-syn* acid (XII) the 1-carboxyl is axial.

These circumstances enable us to make a more rigorous examination of the question of the conformation of *cis-syn*-1,2,3,9,10,10a-hexahydro-7-methoxy-1,2-phenanthrenedicarboxylic acid (XIII) and the peculiarities of its behavior, as described in the preceding communication [1]. It follows from conformational concepts that this geometric isomer can be represented as two conversion forms (A and B).



As will be seen from these spatial models, only the conversion form A is capable of isomerization at the 1-carboxyl with formation of the *trans-anti* acid (II) with a diequatorial disposition of the carboxyls and it should not isomerize at the 2-carboxyl, which is in fact so. If a conversional change of the *cis-syn* acid into form B were possible, then the character of the isomerization of its monoesters would be the opposite and the monoester (III) with a 2-methoxycarbonyl would give the isomeric *trans-syn* acid (XIV) as a result of isomerization at this group. The tendency of only one monoester (IV) with the methoxycarbonyl at C₁ to isomerize shows that the original *cis-syn* acid (XIII) exists preferentially as the conversion form A, which is energetically the more favored because in this form there is an absence of metaaxial interaction between the 2-carboxyl and the ring system, which is present in the conversion form B.

In connection with this conclusion it is necessary to examine the previously observed fact of the inability of the *cis-syn* acid (XIII) to undergo lactonization [1]. It is probable that, despite the presence of an axial carboxyl at C₁ that is formally capable of lactonization, in such a spatial system double-bond displacement is preferred, so that instead of lactonization a shift of the double bond into the intercycle position occurs.

EXPERIMENTAL

***cis-syn* Monoester (III).** The *cis-syn* anhydride (V) (6 g) was added to a solution of sodium (0.5 g) in 100 ml of dry methanol; the mixture was warmed gently (to complete dissolution), was allowed to stand for two minutes, filtered, and poured into 100 ml of water containing an excess of hydrochloric acid. The precipitate of the monoester (III) was separated by centrifugation, washed with water, and dried in air. We obtained 6.32 g of the *cis-syn* monoester (III), m. p. 186-189°, which, after crystallization from isopropyl alcohol, had m. p. 195-196° (decomp.); yield 80%. Found: C 68.37; 68.26; H 6.24; 6.08%. C₁₈H₂₀O₅. Calculated: C 68.33; H 6.37%.

On treatment of the *cis-syn* monoester (III) with ethereal diazomethane we obtained a quantitative yield of the *cis-syn* diester (I), m. p. 116-118°, undepressed by admixture of a known sample [1].

cis-syn Monoester (IV). The cis-syn diester (I) (2.31 g) was added to a solution of potassium hydroxide (0.4 g) in 40 ml of methanol and 10 ml of water, and the mixture was boiled for four hours. Methanol was distilled off, and the residue was diluted with water, filtered, and acidified with hydrochloric acid. The crystals that separated were filtered off, washed with water, and dried. We obtained 1.55 g of the cis-syn monoester (IV), m. p. 190.5-192°, which, after crystallization from acetone, had a constant melting point of 195-196°. A mixture with the cis-syn monoester (III) melted at 170-180°; yield 55%. Found: C 68.67; 68.80; H 6.31; 6.29%. $C_{18}H_{20}O_5$. Calculated: C 68.33; H 6.37%.

Treatment of the cis-syn monoester (IV) with ethereal diazomethane gave the cis-syn diester (I), m. p. 117-118°, undepressed by admixture of the sample prepared as above.

cis-syn-cis Monoester (VI). The cis-syn monoester (III) (8.55 g) was hydrogenated as a suspension in 200 ml of dioxane in presence of 1 g of 30% Pd/SrCO₃ until hydrogen ceased to be absorbed. The catalyst was filtered off, dioxane was vacuum-distilled off, and the crystalline residue was washed on the filter with acetone. We obtained 7.7 g of the cis-syn-cis monoester (VI), m. p. 212-214°. For purification the substance was dissolved in 500 ml of boiling acetone, and the solution was evaporated to one-third bulk; the cis-syn-cis monoester (VI) was then obtained in the form of large clear crystals, m. p. 215-216° (decomp.); yield 85%. Found: C 68.10; 68.01; H 6.99; 6.97%. $C_{18}H_{22}O_5$. Calculated: C 67.90; H 6.97%.

On treatment of the cis-syn-cis monoester (VI) with ethereal diazomethane we obtained a quantitative yield of a cis-syn-cis diester of m. p. 102-103°, undepressed by admixture of the sample described in the preceding communication [1].

cis-syn-cis Monoester (VII). On hydrogenation of 1.0 g of the cis-syn monoester (IV) in presence of 0.1 g of 30% Pd/SrCO₃ in 30 ml of dry dioxane we obtained 0.85 g of the cis-syn-cis monoester (VII), m. p. 172-176°, which after crystallization from methanol melted at 177-178°; yield 75%. Found: C 67.85; 68.00; H 7.04; 7.01%. $C_{18}H_{22}O_5$. Calculated: C 67.90; H 6.97%.

On treatment with an ethereal solution of diazomethane the cis-syn-cis monoester (VII) was converted into the above-described cis-syn-cis diester, m. p. 102-103°.

γ-Lactone (XI). A mixture of 7.97 g of the cis-syn-cis monoester (VI), 10 ml of oxalyl chloride, and 75 ml of dry benzene was boiled until solution was complete (one hour); benzene and excess of oxalyl chloride were distilled off, and the oily residue of acid chloride (VIII) was vacuum-evaporated with benzene three times. To the solution of the resulting acid chloride in 50 ml of dry benzene we added 5 ml of 1-butanethiol and 5 ml of dry pyridine, and the mixture was kept in a sealed glass tube for two days at room temperature (a large amount of pyridine hydrochloride gradually separated). The reaction mixture was treated with 40 ml of water, and the organic layer was washed, first with water, then with 1% sodium hydroxide, then with 1% hydrochloric acid, and finally with water again; it was dried with sodium sulfate. Benzene was distilled off, and the oily residue of the thio ester (IX) was dissolved in a mixture of equal volumes of benzene and petroleum ether and passed through a small column of alumina (20 x 1.5 cm), from which it was eluted by means of the same mixture of solvents.

The thio ester (IX) purified in this way (it amounted to 8.5 g) was dissolved in 250 ml of ethanol, a suspension of 60 g of Raney nickel in 50 ml of alcohol was added, and the mixture was stirred vigorously at room temperature for one hour. Catalyst was filtered off and washed with 100 ml of warm dioxane. Solvents were vacuum-distilled off, and to purify it from polymeric impurities the oily residue was dissolved in 10 ml of benzene, the solution was filtered, and benzene was distilled off. We obtained 6.0 g of the hydroxy ester (X) as a colorless glassy substance.

A solution of 5.5 g of the hydroxy ester (X) in 10 ml of benzene was passed through a column containing 70 g of alumina. After elution with benzene (250 ml), removal of solvent by distillation, and washing of the crystalline residue with 15 ml of methanol, we isolated 3.05 g of the γ-lactone (XI), m. p. 149-155°, which, after two crystallizations from methanol, had a constant melting point of 161-162°. The infrared spectrum of the γ-lactone (XI) contained a carbonyl band characteristic for γ-lactones at 1770 cm⁻¹ (in chloroform). Found: C 74.74; 74.69; H 7.54; 7.67%. $C_{17}H_{20}O_3$. Calculated: C 74.97; H 7.40%.

Dehydrogenation of the γ-Lactone (XI). A mixture of 0.8 g of the γ-lactone (XI) and 1.8 g of finely ground selenium was heated for 20 hours at 320-330°. The reaction product was extracted with 30 ml of boiling benzene, and the solution was filtered and vacuum-evaporated. For purification the residue (0.25 g) was dissolved in ben-

zene and passed through a column of alumina (5 g); elution was with benzene (50 ml). After two crystallizations from methanol the dehydrogenation product was isolated in the form of fine scales, m. p. 131-132°. For 7-methoxy-1-methylphenanthrene (XII) the literature gives m. p. 132-133° [6], 135-136° [7], 133.5-134.5° [8]. Found: C 86.34; H 6.27; H 6.26; 6.28%. $C_{16}H_{14}O$. Calculated: C 86.45; H 6.35%.

With the object of demethylating the product 60 mg of 7-methoxy-1-methylphenanthrene (XII) was boiled for one hour with a mixture of 12 ml of acetic acid and 4 ml of 48% hydrobromic acid in a stream of nitrogen. We obtained 8-methyl-2-phenanthrol, which after crystallization from benzene had m. p. 189-190°. For 8-methyl-2-phenanthrol the literature [8] gives m. p. 190-191°. The acetic ester of 8-methyl-2-phenanthrol was prepared by boiling the phenanthrol with acetic anhydride for six hours; after crystallization from 80% methanol it formed small colorless needles, m. p. 136-137°. According to the literature [8], this acetic ester melts at 135.5-136°.

Action of Sodium Methoxide on the cis-syn Monoester (III). A mixture of 2 g of the cis-syn monoester (III) and 130 ml of a 10% solution of sodium methoxide in methanol was boiled for 25 hours. Methanol was vacuum-distilled off to dryness, the residue was dissolved in 170 ml of water, and the solution was filtered and to effect hydrolysis was evaporated in a porcelain dish on a water bath. The residue of salts was filtered off, washed with methanol, and dissolved in 150 ml of water; the solution was acidified with hydrochloric acid. The crystalline precipitate was separated by centrifugation, washed with water, and dried. We obtained 1.79 g of substance of m. p. 188-191°, which after two crystallizations from methanol had m. p. 218-219°, undepressed by admixture of the cis-syn acid (XIII), which we described previously [1]; the cis-syn diester (I) prepared from this had m. p. 116-118°, also undepressed by admixture of a known sample.

Action of Sodium Methoxide on the cis-syn Monoester (IV). A mixture of 0.35 g of the cis-syn monoester (IV) and 30 ml of a 10% solution of sodium methoxide in methanol was boiled for 15 hours and then treated as described above. We isolated 0.27 g of the trans-anti acid (II), m. p. 214-215°, which after crystallization from dioxane had m. p. 221-222°, undepressed by admixture of the sample that we synthesized previously [1].

SUMMARY

1. The isomeric cis-syn monoesters (III) and (IV) were synthesized and their structures were proved. Their isomerization with sodium methoxide was studied, and this made it possible to confirm the configuration of the previously described trans-anti acid (II).
2. An examination was made of the question of the conformation of cis-syn-1,2,3,9;10,10a-hexahydro-7-methoxy-1,2-phenanthrenedicarboxylic acid and its transformation products.

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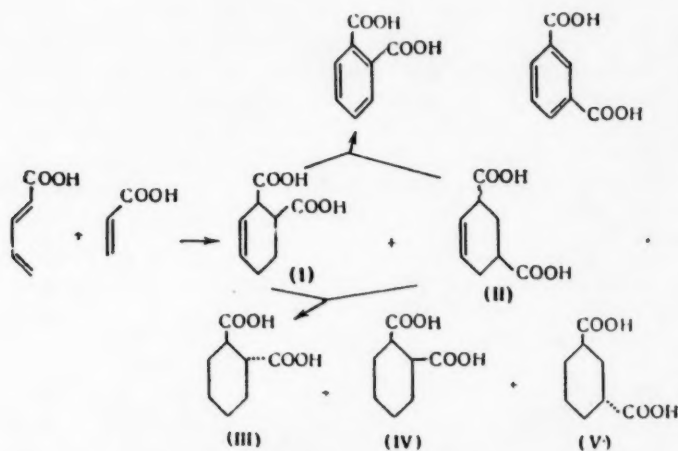
STRUCTURAL ORIENTATION IN THE DIENE CONDENSATION OF 2,4-PENTADIENOIC ACID WITH ACRYLIC ACID AND WITH STYRENE*

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 10, pp. 1810-1814, October, 1960
Original article submitted May 13, 1959

In most of the diene condensations studied the diene component has a donor substituent (alkyl, aryl, alkoxy, etc.). Many fewer dienes containing acceptor substituents have been studied. Thus, structural orientation in the diene condensations of 2,4-pentadienoic acid has been studied only for the case of the reaction with acrylic acid [1]. From the mixture of adducts formed *trans* and *cis* isomers of the *ortho* series were isolated in the ratio of 10 : 1. In this work no *meta* adduct was detected.

As dienophiles in condensations with 2,4-pentadienoic acid we chose acrylic acid and styrene, since the presence of an acceptor substituent in the first of these compounds and the presence of a donor substituent in the second permitted a study of the effect of the electronic character of the substituents on the proportions of structural isomers. We carried out the condensation of 2,4-pentadienoic acid with acrylic acid under the conditions described by Alder [1] (150°, 6 hours) and obtained an 86% yield of a mixture of the *ortho* and *meta* adducts (I) and (II):



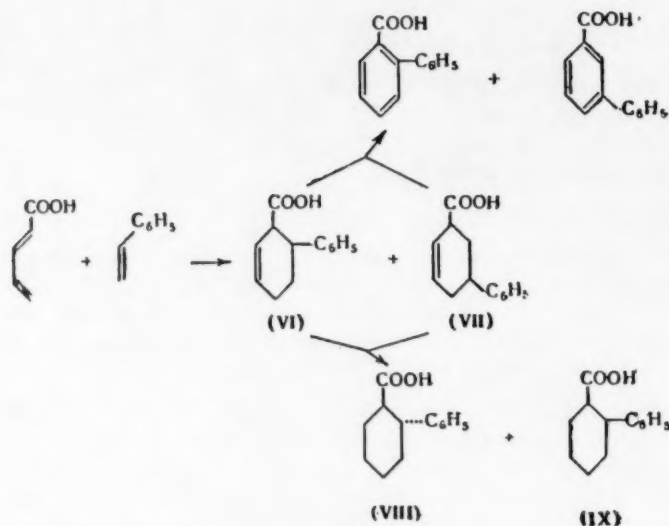
The mixture of adducts was esterified by boiling it in methanol in presence of hydrochloric acid, and the resulting methyl esters were dehydrogenated over 15% palladium-charcoal. Hydrolysis of the dehydrogenation products with a methanolic solution of sodium hydroxide gave a mixture of benzenedicarboxylic acids. By sepa-

* This work forms a continuation of an investigation of the laws governing the diene synthesis, which was begun under the supervision of I. N. Nazarov.

ration of this mixture by selective extraction with hot water,* we obtained phthalic and isophthalic acids, the ratio of which (8.8 : 1) corresponded to the ratio of ortho and meta isomers (I) and (II) in the original mixture of adducts.

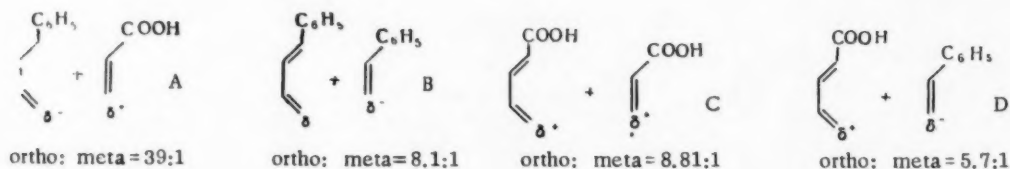
The relative amounts of stereoisomers were determined after the hydrogenation of the adducts over an Adams platinum catalyst. By crystallization and chromatography on alumina we succeeded in separating trans-ortho (III) and cis-ortho (IV) isomers from the hydrogenated mixture in the ratio of 8.6 : 1. We obtained also an acid of m. p. 145-147°, which appeared to correspond to the trans-meta isomer (V) and amounted to about 3% of the mixture being separated.

The condensation of 2,4-pentadienoic acid with styrene was carried out under the same conditions: heating a mixture of diene and dienophile at 150° for six hours. We obtained a 58% yield of a mixture of the adducts (VI) and (VII).



By esterification, dehydrogenation over palladized charcoal, and subsequent hydrolysis, the adducts (VI) and (VII) were converted into a mixture of biphenylcarboxylic acids. From this by fractional crystallization we succeeded in isolating 2- and 3-biphenylcarboxylic acids, the ratio of which (5.7 : 1) corresponded to the ratio of ortho and meta isomers (VI) and (VII) in the original mixture of adducts. Hydrogenation of the adducts over an Adams platinum catalyst and fractional crystallization of the products permitted the separation of trans-ortho (VIII) and cis-ortho (IX) isomers in the ratio of 17 : 1. The identities of the adducts were proved by mixture melting point tests with the hydrogenation products from the adducts formed by 1-phenyl-1,3-butadiene with acrylic acid, for which the steric configurations have been proved [2]. In this case we were unable to isolate stereoisomers corresponding to the meta adduct (VII).

With the aid of the results of a previous investigation [3] we studied structural orientation for all possible combinations of the positions of the phenyl and carboxyl substituents in the dienophile and in the 1-position of the diene. We give the results below.



* At 99° 100 g of water dissolves 18 g of phthalic and only 0.2 g of isophthalic acid.

According to various variants of the ionoid mechanism of the diene synthesis [4, 5] when the polarities of the ends of the diene and dienophile molecules differ [A and D] the ortho isomer should be formed preferentially, whereas in the case of identical polarities (B and C) the meta isomer should be formed preferentially. However, we have shown that in all these cases the ortho isomer predominates in the mixture of adducts obtained. This excludes the possibility of the polarity of molecules playing a determining role in structural orientation in the diene synthesis, and it contradicts the ionoid mechanism for this reaction.

However, the nature of the substituents affects the relative amounts of structural isomers in a definite way. Thus, with a donor substituent in the diene and an acceptor in the dienophile (A) the proportion of meta isomer in the mixture of adducts is only 2-3%. When the polarities coincide (B and C), the amount of meta isomer increases to 10-11%. Finally, with the acceptor substituent in the diene and the donor in the dienophile (D) the structural orientation is still less selective and the amount of meta isomer attains 15%. Hence, structural orientation becomes somewhat less selective on introduction of an acceptor substituent in the diene or a donor in the dienophile, and becomes more selective when a donor is present in the diene and an acceptor substituent in the dienophile. It is interesting that an analogous phenomenon is found in the kinetics of the diene synthesis: reaction is speeded up by the introduction of donor substituents in the diene or acceptor substituents in the dienophile [6,8]. The possibility cannot be excluded that this is due to the differing roles of the diene and dienophile in the diene synthesis.

EXPERIMENTAL

2,4-Pentadienoic acid (m. p. 68-70°) was synthesized by Kohler and Butler's method [9]. Acrylic acid (b. p. 141-142°) and styrene (b. p. 145-146°) were distilled commercial products. For the chromatographic separation of the products we used commercial "alumina for chromatography", which had a Brockmann activity [10] of not less than 2 units.

Condensation of 2,4-Pentadienoic Acid with Acrylic Acid. A mixture of 25 g of 2,4-pentadienoic acid, 25 g of acrylic acid, and 0.1 g of hydroquinone was heated at 150° for six hours in a flask fitted with reflux condenser. Vacuum fractionation gave 37.2 g (86%) of a mixture of the adducts (I) and (II), b. p. 170-175° (35 mm). The mixture partially crystallized out. Found: C 56.17; 56.29; H 5.87; 5.90%, $C_8H_{10}O_4$. Calculated: C 56.46; H 5.92%.

The mixture of adducts (15 g) was esterified by boiling it with 100 ml of methanol containing 0.1 ml of concentrated hydrochloric acid for 12 hours. The reaction products were neutralized with sodium carbonate, methanol was distilled off, and the residue was vacuum-fractionated. We obtained 16.1 g (92%) of a mixture of methyl esters, b. p. 181-186° (17 mm).

The 16.1 g of methyl esters was dehydrogenated by repeated passage over 15% palladized charcoal at 340-360°. We obtained 13.2 g (84%) of dehydrogenation products (n_D^{18} 1.5140), the hydrolysis of which with excess of 10% methanolic sodium hydroxide gave 10.2 g (91%) of benzenedicarboxylic acids. On separation of the latter by selective extraction with hot water we isolated 7.9 g of phthalic acid, m. p. 190-191°, and 0.9 g of isophthalic acid, the dimethyl ester of which had m. p. 64-65°. Neither substance showed depression of melting point in admixture with a known sample. The ortho : meta ratio was 8.8 : 1.

The mixture of adducts (10.5 g) was hydrogenated as a solution in 50 ml of ethanol in presence of 0.1 g of platinum (from platinum dioxide). In the course of 4.5 hours 1520 ml of hydrogen was absorbed (the theoretical amount was 1500 ml at 750 mm and 20°). The catalyst was filtered off, and ethanol was distilled from the filtrate under reduced pressure. We obtained 9.9 g (95%) of a mixture of hydrogenation products.

The acids obtained were separated by crystallization from an ether-hexane mixture. The liquid residue was subjected to chromatography on alumina (20 ml of absorbent to 1 g of mixture; elution with 0.5-2% hydrochloric acid); the crystalline products from the chromatographic treatment were again subjected to fractional crystallization. In this way from 5.6 g of hydrogenation products we obtained 4.3 g of trans-1,2-cyclohexanedicarboxylic acid (III), m.p. 215-217°, and 0.5 g of cis-1, 2-cyclohexanedicarboxylic acid (IV), m.p. 187-189°; neither acid showed depression of melting point in admixture with a known sample. We isolated also 0.15 g of an acid of m.p. 145-147°, the constants of which corresponded to trans-1, 3-cyclohexanedicarboxylic acid (the literature [11] gives m.p. 148°). The ratio of the amounts of trans-ortho and cis-ortho isomers (III) and (IV) was 8.6 : 1.

Condensation of 2,4-Pentadienoic Acid with Styrene. A mixture of 20 g of 2,4-pentadienoic acid, 40 g of styrene, and 0.1 g of hydroquinone was heated at 150° for six hours in a flask fitted with reflux condenser. Vacuum fractionation of the reaction products gave 24 g (58%) of a partially crystallized mixture of the adducts (VI) and (VII), b. p. 220-225° (25 mm). Found: C 76.99; 77.15; H 6.88; 6.92%. $C_{13}H_{14}O_2$. Calculated: C 77.20; H 6.98%.

The mixture of acids (17 g) was esterified by boiling it for ten hours with 100 ml of methanol containing 0.1 ml of concentrated hydrochloric acid. The products were neutralized with sodium carbonate, methanol was distilled off, and vacuum distillation of the residue gave 16.8 g (92%) of methyl esters, b. p. 162-164° (15 mm). Dehydrogenation of the latter over 15% palladized charcoal at 340-360° gave 14.5 g (88%) of a mixture of dehydrogenation products having n_D^{15} 1.5706. Hydrolysis of 14 g of this mixture with excess of a 10% methanolic solution of sodium hydroxide gave 10.6 g (81%) of a mixture of biphenylcarboxylic acids; from the neutral fraction we isolated 0.3 g of biphenyl, m. p. 68-69°, undepressed by admixture of a known sample.

The mixture of acids (5.4 g) was separated by crystallization from acetone and an ether-hexane mixture; we then obtained 4 g of 2-biphenylcarboxylic acid, m. p. 111-112°, and 0.7 g of 3-biphenylcarboxylic acid, m. p. 162-163°; neither acid showed depression of melting point in admixture with a known sample. The ortho-meta ratio was 5.7 : 1.

The mixture of adducts (13 g) was hydrogenated as a solution in 75 ml of ethanol in presence of 0.1 g of platinum (from platinum dioxide). In the course of four hours 1530 ml of hydrogen was absorbed (the theoretical amount was 1510 ml at 747 mm and 23°). The catalyst was filtered off, and ethanol was distilled from the filtrate under reduced pressure (about 20 mm). We obtained 12.7 g (98%) of a mixture of hydrogenation products. From the hydrogenation products by crystallization from acetone and an ether-hexane mixture we isolated 10.3 g of trans-2-phenylcyclohexanecarboxylic acid (VIII), m. p. 105-106°, and 0.6 g of cis-2-phenylcyclohexanecarboxylic acid (IX), m. p. 75-76°. Neither acid showed depression of melting point in admixture with a sample prepared by the hydrogenation of the corresponding adduct formed by 1-phenyl-1,3-butadiene with acrylic acid. The ratio of the amounts of trans-ortho and cis-ortho isomers (VIII) and (IX) was 17 : 1.

Hydrogenation of the Adducts Formed by 1-Phenyl-1,3-butadiene with Acrylic Acid [3]. trans-2-Phenyl-3-cyclohexene-1-carboxylic acid (m. p. 104-104.5°) (1 g) was hydrogenated as a solution in 20 ml of ethanol in presence of 0.05 g of platinum (from platinum dioxide). In the course of three hours 131 ml of hydrogen was absorbed (the theoretical amount was 126 ml at 21° and 765 mm). The catalyst was filtered off, and ethanol was distilled off under reduced pressure. We obtained 0.95 g (96%) of trans-2-phenylcyclohexanecarboxylic acid (VIII), m. p. 105.5-106°.

On hydrogenation of 1 g of cis-2-phenyl-3-cyclohexene-1-carboxylic acid (m. p. 119-120°) under the same conditions we obtained 0.97 g (98%) of cis-2-phenylcyclohexanecarboxylic acid (IX), m. p. 75-76°.

SUMMARY

1. The condensations of 2,4-pentadienoic acid with acrylic acid and with styrene were carried out; structural isomers were isolated from the reaction products, and their proportions were determined. In both cases there was a great predominance of ortho adducts, mainly the trans isomers.
2. The polarities arising from the introduction of substituents into the diene and dienophile molecules do not constitute a determining factor in structural orientation in the diene synthesis.

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STRUCTURAL ORIENTATION IN THE DIENE CONDENSATIONS OF
2-METHOXY-1,3-BUTADIENE AND OF CHLOROPRENE WITH
UNSYMMETRICAL DIENOPHILES*

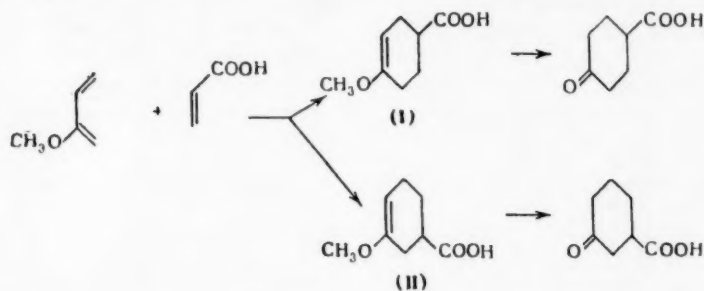
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 10, pp. 1815-1819, October, 1960
Original article submitted May 13, 1959

The relative amounts of structural isomers formed in diene condensations of unsymmetrically substituted dienes with unsymmetrical dienophiles depend on the natures of the substituents in both addends. In the present work these relations were investigated for the condensations of 2-methoxy-1,3-butadiene and of chloroprene with acrylic acid and with styrene.

The condensation of 2-alkoxy-1,3-butadienes with various unsymmetrical dienophiles has been treated extensively in the literature. The formation of para adducts was proved for condensations with acrolein [1, 2], vinyl ketones [3, 4], ethynyl ketones [5], the esters and nitriles of acrylic and methacrylic acids [6, 7], tetrollic ester [8], mesaconic ester [9], and citraconic anhydride [9]. However, the isolation of the second structural isomer, the meta adduct, was effected in only one case: the condensation of 2-methoxy-1,3-butadiene with 2-methyl-2-cyclohexen-1-one at 260-270°. Under these conditions the ratio of the amounts of para and meta isomers was about 6 : 1 [10].

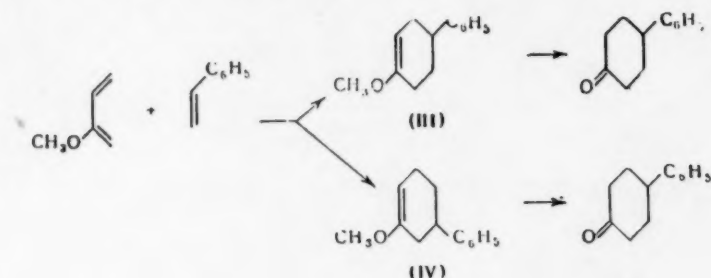
We carried out the diene condensations by heating a mixture of diene and dienophile, mixed with benzene, in steel tubes in presence of 0.1-0.2% of hydroquinone as a polymerization inhibitor. Heating of 2-methoxy-1,3-butadiene with acrylic acid at 150° for ten hours led to a 72% yield of a mixture of the adducts (I) and (II):



On hydrolysis of the adducts by means of 3% hydrochloric acid we obtained a mixture of oxocyclohexanecarboxylic acids. We were able to separate these by crystallization and chromatography on alumina. We then obtained 4- and 3-oxocyclohexanecarboxylic acids in relative amounts of 8 : 1, which will be the ratio of the amounts of para (I) and meta (II) isomers in the original mixture of adducts.

* This work forms a continuation of investigations begun under the supervision of I. N. Nazarov.

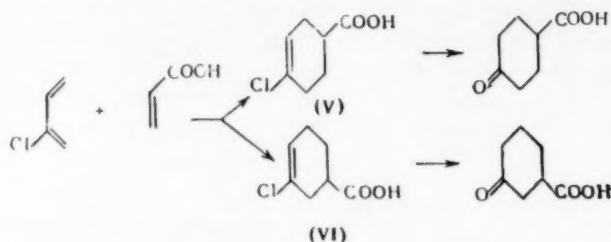
The condensation of 2-methoxy-1,3-butadiene with styrene, which was carried out under the same conditions, gave a 59% yield of the mixture of adducts (III) and (IV):



Hydrolysis of the adducts with 3% hydrochloric acid led to a mixture of phenylcyclohexanones. By chromatography of this mixture on alumina we isolated solid 4-phenylcyclohexanone and liquid 3-phenylcyclohexanone. The ratio of the amounts (12 : 1) corresponds to the relative contents of para (III) and meta (IV) isomers in the mixture of adducts obtained.

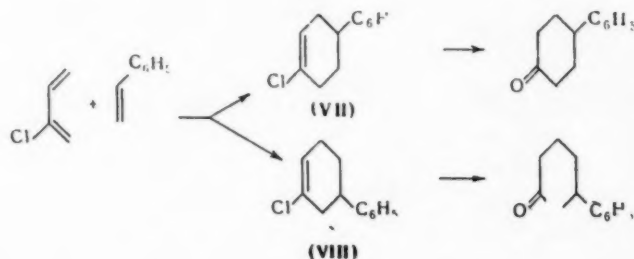
Until now it has been considered that the reactions of chloroprene with unsymmetrical dienophiles proceed strictly selectively with formation of only para adducts. The structure of the para adduct was proved in the condensation of chloroprene with acrylic acid and its derivatives [7, 11, 12], acrolein [13], vinyl and ethynyl ketones [4, 13], and propiolonitrile [14].

The reaction of chloroprene with acrylic acid, which was carried out by heating the reactants together at 150° for five hours, gave an 83% yield of a mixture of the adducts (V) and (VI):



The hydrolysis of compounds containing chlorine at the double bond requires much more severe conditions than the analogous reaction with compounds having a methoxy group at the double bond. The mixture of the adducts (V) and (VI) could be hydrolyzed only with concentrated sulfuric acid at 0° . The oxocyclohexanecarboxylic acids then obtained were separated, as in the condensation with 2-methoxy-1,3-butadiene, by crystallization and chromatography on alumina. The ratio of the amounts of 4- and 3-oxocyclohexanecarboxylic acids so found was 9.3 : 1.

Condensation of chloroprene with styrene at 150° for 12 hours gave a mixture of the adducts (VII) and (VIII) in 20% yield.



As in the previous case, the hydrolysis of the adducts was carried out by means of concentrated sulfuric acid at 0°, when a mixture of phenylcyclohexanones was obtained. On chromatography of the latter on alumina we isolated 4-phenylcyclohexanone, corresponding to (VII), and 3-phenylcyclohexanone, corresponding to (VIII), in the proportions of 14.4 : 1.

We showed, therefore, that in all the condensations of 2-methoxy-1,3-butadiene and chloroprene investigated a mixture of both possible structural isomers was formed, and in this the para adduct was present in greatly preponderating amount. In the reactions investigated the proportion of meta adduct formed did not vary substantially. However, the structural orientation was somewhat more specific for chloroprene than for 2-methoxy-1,3-butadiene and for styrene than for acrylic acid. This absence of any substantial difference in the proportions of structural isomers for dienes and dienophiles containing substituents of different types may be regarded as an argument in favor of a homolytic mechanism for the diene synthesis.

EXPERIMENTAL

2-Methoxy-1,3-butadiene (b. p. 75-76°; n_D^{20} 1.4435) was prepared by the pyrolysis of 1,1,3-trimethoxybutane over potassium hydrogen sulfate [10]. Chloroprene (b. p. 59-60°; n_D^{15} 1.4600), acrylic acid (b. p. 140-141°; n_D^{17} 1.4231), and styrene (b. p. 145-146°; n_D^{20} 1.5425) were distilled commercial products. For the chromatographic separation of products we used commercial "alumina for chromatography", which had a Brockmann activity [15] of not less than 2 units. The diene condensations were carried out in a 150-ml steel tube.

Condensation of 2-Methoxy-1,3-butadiene with Acrylic Acid. A mixture of 12 g of 2-methoxy-1,3-butadiene, 14 g of acrylic acid, 0.1 g of hydroquinone, and 50 ml of benzene was heated at 150° for ten hours. Vacuum fractionation gave 16 g (72%) of mixture of the adducts (I) and (II), b. p. 151-155° (12 mm) and n_D^{20} 1.4722. Found: C 61.34; 61.47; H 7.74; 7.68%. $C_8H_{12}O_3$. Calculated: C 61.52; H 7.75%.

The mixture of adducts (I) and (II) (6.2 g) was stirred with 30 ml of 3% hydrochloric acid for one hour at room temperature. The reaction products were extracted with ether in a percolator for ten hours; the ether extract was dried with calcium chloride, and ether was distilled off. We obtained 5.5 g (97%) of a mixture of oxocyclohexanecarboxylic acids, which were separated by fractional crystallization from a hexane-ether mixture. The liquid residue was subjected to chromatography on alumina (20 ml of adsorbent per gram of mixture; elution with 0.5-2% hydrochloric acid), after which the crystalline chromatography products were again subject to fractional crystallization. In this way, from 3.2 g of acids we obtained 2.4 g of 4-oxocyclohexanecarboxylic acid, m. p. 66-67°, the semicarbazone of which had m. p. 194-196° (the literature gives m. p. 67-68, semicarbazone m. p. 194° [16]). We isolated also 0.3 g of 3-oxocyclohexanecarboxylic acid (corresponding to the meta adduct), m. p. 73-75°, the semicarbazone of which had m. p. 182-183° (the literature [17] gives m. p. 75-76°, semicarbazone m. p. 182-183°). The ratio of the amounts of para and meta isomers was 8 : 1.

Condensation of 2-Methoxy-1,3-butadiene with Styrene. A mixture of 19 g of 2-methoxy-1,3-butadiene, 25 g of styrene, 0.1 g of hydroquinone, and 50 ml of benzene was heated at 150° for ten hours. Vacuum fractionation gave 25 g (59%) of mixture of the adducts (III) and (IV), b. p. 140-145° (12 mm) and n_D^{20} 1.5170. Found: C 82.70; 82.81; H 8.52; 8.57%. $C_{13}H_{16}O$. Calculated: C 82.93; H 8.57%.

The mixture of adducts (III) and (IV) 22.3 g) was stirred with 85 ml of 3% hydrochloric acid at room temperature for three hours. The reaction products were extracted with ether (three portions of 200 ml), and the ether extract was dried over anhydrous calcium chloride. Ether was distilled off, and vacuum distillation of the residue gave 18 g (88%) of a mixture of phenylcyclohexanones, b. p. 150-155° (11 mm).

The mixture of ketones (5.3 g) was subjected to chromatography on 250 ml of alumina (elution with hexane-benzene). We obtained 4.2 g of 4-phenylcyclohexanone (corresponding to the para isomer), m. p. 78-79°, the 2,4-dinitrophenylhydrazone of which had m. p. 194-195° (the literature [18] gives m. p. of ketone 76-78°). We isolated also 0.35 g of liquid 3-phenylcyclohexanone (corresponding to the meta adduct), the 2,4-dinitrophenylhydrazone of which had m. p. 181-183°, undepressed by admixture of a known sample (prepared according to [19]). The ratio of the amounts of para and meta isomers was 12 : 1.

Condensation of Chloroprene with Acrylic Acid. A mixture of 22 g of chloroprene, 20 g of acrylic acid, 0.1 g of hydroquinone, and 60 ml of benzene was heated at 150° for five hours. Benzene was distilled off, and the residue was vacuum-distilled. We obtained 33.4 g (83%) of a mixture of the adducts (V) and (VI), b. p. 162-165° (17 mm). The adducts crystallized completely. Found: C 52.30; 52.24; H 5.57; 5.61%. C_7H_9Cl . Calculated: C 52.33; H 5.66%.

The mixture of the adducts (V) and (VI) (30.5 g) was added in portions to 80 ml of concentrated sulfuric acid, which was stirred vigorously in a flask cooled with ice. Vigorous liberation of hydrogen chloride soon began. When the addition was complete (20 minutes), the mixture was stirred further for two hours with cooling and then left overnight at room temperature. On the next day the mixture was poured onto 200 g of ice, and 125 g of sodium carbonate was added to the resulting solution. The acids liberated were extracted with ether in a percolator for ten hours, and the ether extract was dried over anhydrous calcium chloride. Ether was distilled off, and vacuum distillation of the residue gave 22.2 g (82%) of a mixture of oxocyclohexanecarboxylic acids, b. p. 200-205° (25 mm). By crystallization from a hexane-ether mixture and chromatography on alumina (as described for the condensation of 2-methoxy-1,3-butadiene with acrylic acid), from the mixture of keto acids we isolated 17.7 g of 4-oxocyclohexanecarboxylic acid, m. p. 66-67°; semicarbazone, m. p. 194-196°. We obtained also 1.9 g of 3-oxocyclohexanecarboxylic acid (corresponding to the meta adduct), m. p. 182-183°. The ratio of the amounts of para and meta isomers was 9,3 : 1.

Condensation of Chloroprene with Styrene. A mixture of 22 g of chloroprene, 30 g of styrene, 0.1 g of hydroquinone, and 60 ml of benzene was heated at 150° for 12 hours. Vacuum fractionation gave 9.7 g (20%) of a mixture of the adducts (VII) and (VIII) as a liquid that darkened rapidly in air, b. p. 130-134° (8 mm) and n_D^{16} 1.5560. We did not succeed in obtaining an analytically pure sample of the adducts.

The mixture of the adducts (VII) and (VIII) (7 g) was added over a period of two minutes to vigorously stirred concentrated sulfuric acid (15 ml) cooled with an ice-salt mixture. The mixture was stirred with the same cooling for two hours further and was then poured onto 100 g of crushed ice. The mixture was partially neutralized with 30 g of sodium carbonate, the reaction products were extracted with ether (five portions of 100 ml), and the ether extract was dried with calcium chloride. Ether was distilled off, and vacuum distillation of the residue gave 4.2 g (67%) of a mixture of phenylcyclohexanones, b. p. 157-161° (15 mm).

By chromatography of 4.3 g of the mixture of ketones on 200 ml of alumina (elution with hexane and benzene) we obtained 3.60 g of 4-phenylcyclohexanone, corresponding to the para adduct, m. p. 78-79°; 2,4-dinitrophenylhydrazone, m. p. 194-195°. We isolated also 0.25 g of liquid 3-phenylcyclohexanone (corresponding to the meta adduct); 2,4-dinitrophenylhydrazone, m. p. 181-183°, undepressed by admixture of a known sample. The ratio of the amounts of para and meta isomers was 14.4 : 1.

SUMMARY

1. The diene condensations of 2-methoxy-1,3-butadiene and of chloroprene with acrylic acid and with styrene were carried out; in all cases both para and meta isomers were isolated from the mixture of adducts, and their relative amounts were determined.

2. The relative amounts of the structural isomers indicate that a methoxy group in the 2-position of the diene has a less marked directing effect than chlorine. Carboxyl in the dienophile is a less powerful orientant than phenyl.

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SYNTHESIS OF 1-ARYL-4-DIMETHYLAMINO-1-BUTANOLS AND THEIR ESTERS

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

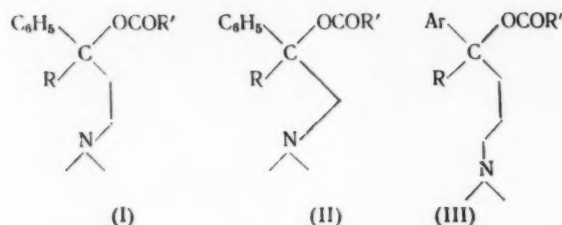
No. 10, pp. 1820-1824, October, 1960

Original article submitted May 21, 1959

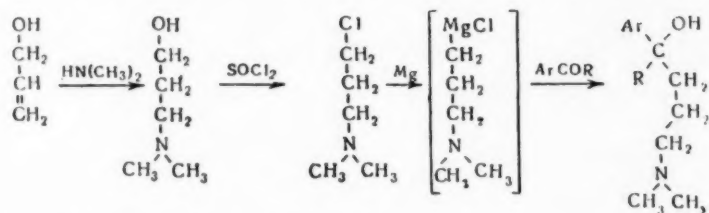
According to the literature, the physiological properties of procaine analogs and some related compounds depend on the length of the methylene chain of the amino alcohol. Thus, according to Burnett and others [1] increase in the number of CH_2 groups from two to five (from procaine to 5-diethylaminopentyl p-aminobenzoate) leads to an increase in its local anesthetic properties and also in its toxicity. Other authors [2] showed that the trimethylene chain had the highest activity, and they did not find any appreciable increase in activity on lengthening the chain to six carbon atoms.

Recently [3], a substantial increase in anesthetic activity has been noted in analogs of other compounds similar to procaine in structure on passage from a di- to a tri-methylene chain.

We have been occupied in recent years with an investigation on the esters of 3-amino-1-propanols (I) [4], and have also tried to determine the effect of change in the length of the methylene chain of the amino alcohol on the physiological properties of the compounds in which we were interested. With this object we have previously synthesized a series of 2-dimethylamino-1-phenylethyl esters (II) [5]. The present paper reports the synthesis of 1-aryl-4-dimethylamino-1-butanols (III) and some of their esters, on which there is little information in the literature.



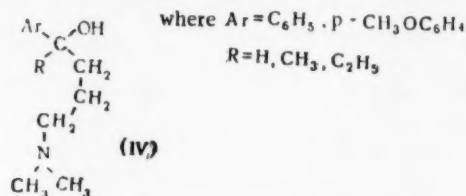
The required aminobutanols were prepared by a four-stage synthesis, which may be represented as follows:



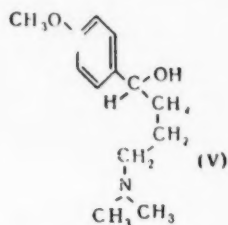
* This work was commenced during the lifetime of I. N. Nazarov.

The least studied reaction in this scheme was Marxer's reaction between a haloalkylamine and magnesium [6].

We modified this reaction somewhat: we made a clear separation between the process of preparing the Grignard reagent and the reaction of the latter with the carbonyl compound, whereas Marxer almost combines the two stages together, which makes the already difficult reaction of the haloalkylamine with magnesium still more difficult. We found also that the ethyl bromide used as an activator must be added before the haloalkylamine. Otherwise, the ethyl bromide is bound by the haloalkylamine with formation of the quaternary salt. The Grignard reagent obtained forms a semisolid ether-insoluble mass, a circumstance which naturally makes reaction with the carbonyl compound more difficult. A little dry benzene, which may be added before the addition of the carbonyl compound or together with it, liquefies the semisolid Grignard reagent and facilitates the mixing of the two reactants. As regards the modifications suggested by Breslow and co-workers [7] (passage of dry nitrogen and use of a magnesium-copper alloy as activator), in our opinion these only complicate the procedure in the reaction without affording any advantages. The series of aminobutanols (IV) obtained by the above-described reaction is presented in Table 1, and as a typical example we describe the preparation of 4-dimethylamino-1-phenyl-1-butanol (IV) ($R = H$, $Ar = C_6H_5$).



We attempted to prepare esters of these aminobutanols by acylation of the amino alcohol base with acid chlorides in dry benzene. Under these conditions we obtained esters of only the secondary amino alcohol 4-dimethylamino-1-phenyl-1-butanol. As regards the other amino alcohols of this series, in spite of the use of various acylation methods, we did not succeed in obtaining their esters. A very unusual circumstance was the formation in low yield of only the benzoic ester of 4-dimethylamino-1-methyl-1-butanol, while others esters of this alcohol could not be obtained. As regards the other secondary amino butanol (V)



the difficulties in esterification may be due to the presence of a methoxy group in the para position. We noted analogous difficulties due to a para-methoxyl in a previous investigation [8].

Further, in order to examine changes in pharmacological action of the substances due to conversion of a tertiary nitrogen into quaternary [9], in some cases we prepared so-called "pairs": hydrochlorides and methyl methosulfates. The ester hydrochlorides synthesized (III) are presented in Table 2, and as a typical example a description is given of the preparation of 4-dimethylamino-1-phenylbutyl benzoate hydrochloride (III) ($R = H$, $Ar = C_6H_5$, $R' = C_6H_5$). Some of the compounds synthesized are undergoing pharmacological tests in Professor M. Ya. Mikhel'son's laboratory at the Institute of Evolutionary Physiology of the Academy of Sciences of the USSR and in the Pharmacology Department of the Leningrad Medical Institute. The results of the tests will be published separately.

Also, 4-dimethylamino-1-methyl-1-phenyl-1-butanol hydrochloride was tested** in natural rubber mixes.

* This work was commenced during the lifetime of I. N. Nazarov.

** In the Research Institute for the Chemical Industry.

TABLE 1

$\begin{array}{c} \text{Ar} \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2 \end{array}$						
	R=H Ar=C ₆ H ₅	R=CH ₃ Ar=C ₆ H ₅	R=C ₂ H ₅ Ar=C ₆ H ₅ *	R=H Ar=p-CH ₃ OC ₆ H ₄	R=CH ₃ Ar=p-CH ₃ OC ₆ H ₄	R=C ₂ H ₅ Ar=p-CH ₃ OC ₆ H ₄
Molecular formula	C ₁₂ H ₁₉ ON	C ₁₃ H ₂₁ ON	C ₁₄ H ₂₃ ON	C ₁₃ H ₂₁ O ₂ N	C ₁₄ H ₂₃ O ₂ N	C ₁₅ H ₂₅ O ₂ N
Yield, %	71,7	55,5	73,9	64,9	33,4	39,6
B. p. (°C at 1 mm)	101—103	92—93	102—104	135—136	123—125	123—124
M.p. (°C)	49—50	—	44—46	—	—	40—42
n_D^{20}	1,5196	1,5140	—	1,5247	1,5233	1,5166
d_4^{20}	—	0,9728	—	1,0301	1,0192	—
Found	MR	—	64,10	—	66,31	71,01
	%C	—	75,10 75,02	—	69,78 69,71	70,62 70,61
	%H	—	10,23 10,15	—	9,40 9,37	9,62 9,59
	%N	7,39 7,22	6,98 6,92	6,53 6,45	6,39 6,29	6,19 6,12
Calculated	MR	—	64,10	—	65,74	70,36
	%C	—	75,31	—	69,92	70,84
	%H	—	10,21	—	9,48	9,77
	%N	7,25	6,76	6,33	6,27	5,90
Content of active hydrogen according to the Tserévitinov-Chugaev method						
	1,04	0,90	—	0,99	1,03	0,98
Hydrochloride	Molecular formula	C ₁₂ H ₂₀ ONCl	C ₁₃ H ₂₂ ONCl	C ₁₄ H ₂₄ ONCl	C ₁₃ H ₂₂ O ₂ NCl	C ₁₄ H ₂₄ O ₂ NCl
	M.p. (°C)	75,5—78	141—143,5	176—177,5	161,5—162	173,5—174,5
	Found % N	—	5,65 5,76	5,43 5,47	5,38 5,10	4,81 5,11
	Calculated % N	—	5,75	5,43	5,39	5,12

* Methyl methosulfate: m. p. 114.5–115.5°C. Found: N 4.32; 4.09%, C₁₆H₂₉O₅SN. Calculated: N 4.03%.

TABLE 2

Ester hydrochloride	Molecular formula	Yield %	M. p. (°C)	Found N %	Calculated N %
R = H Ar = C ₆ H ₅ * R' = C ₂ H ₅	C ₁₁ H ₁₄ O ₂ NCl	77,9	112—113	5,28 4,98	4,90
R = H Ar = C ₆ H ₅ ** R' = C ₂ H ₅	C ₁₀ H ₁₄ O ₂ NCl	52,2	136—138	3,99 3,90	4,19
R = H Ar = C ₆ H ₅ R' = CH ₂ OC ₂ H ₅	C ₂₂ H ₂₈ O ₃ NCl	74,4	139—141	3,84 3,91	3,85
R = H Ar = C ₆ H ₅ R' = CH ₂ CH ₂ OC ₂ H ₅	C ₂₁ H ₂₈ O ₃ NCl	65,2	91—92	3,70 3,69	3,71
R = H Ar = C ₆ H ₅ R' = CH ₂ SC ₂ H ₅	C ₂₀ H ₂₆ O ₂ SNCl	59,9	106—108	3,70 3,41	3,69
R = CH ₃ Ar = C ₆ H ₅ R' = C ₂ H ₅	C ₂₃ H ₂₈ O ₂ NCl	3,4	155—156,5	3,88 4,06	4,03

* Methyl methosulfate: m.p. 140—141,5°. Found: N 3,94; 3,99%. C₁₇H₂₀O₆SN. Calculated: N 3,73%.

** Found: Cl 10,77%; Calculated: Cl 10,62%.

This compound was found to be a secondary vulcanization accelerator for rubber; it activates mercaptobenzo-thiazole (Captax) and its use in conjunction with the latter permits the preparation of vulcanized rubbers of adequate strength and elasticity.

EXPERIMENTAL

The original 3-chloro-N,N-dimethylpropylamine was prepared from 3-dimethylamino-1-propanol, which was itself prepared from allyl alcohol and liquefied dimethylamine in an autoclave in presence of dry sodium hydroxide [10].

4-Dimethylamino-1-phenyl-1-butanol [6] (IV) (R = H, Ar = C₆H₅). A mixture of 5.2 g (0.214 g-atom) of magnesium powder and 30 ml of dry ether was introduced into a flask fitted with stirrer, reflux condenser, dropping funnel, and thermometer; a small crystal of iodine was added. The mixture was warmed to 30°, and 1 ml of ethyl bromide was added. When the reaction between magnesium and ethyl bromide was complete, the mixture was boiled gently and over a period of 30 minutes 24.6 g (0.202 mole) of 3-chloro-N,N-dimethylpropylamine (freshly distilled at 79–80° under 145 mm) in 25 ml of dry ether was added dropwise. The reaction mixture was boiled until most of the magnesium had disappeared, after which the thick mass was thinned down by the addition of 50 ml of dry benzene and cooled to room temperature. With vigorous stirring gradual addition was made of 22.1 g (0.208 mole) of benzaldehyde in 50 ml of dry benzene.

The reaction mixture was stirred in the cold for one hour, and on the next day it was stirred further for 90 minutes at 45–47°. It was then decomposed under cooling with aqueous ammonium chloride and was acidified to congo red with 1 : 1 hydrochloric acid. Neutral products were extracted with several portions of ether, and the aqueous layer was made alkaline, first with ammonia and then with caustic alkali. The base liberated was repeatedly extracted with ether. The ether extracts of the basic products were dried with sodium sulfate, ether was distilled off, and the residue was vacuum-distilled. We obtained 28.0 g (71.7%) of 4-dimethylamino-1-phenyl-1-butanol, b. p. 101–103° (1 mm) and n_D^{20} 1.5196. When allowed to stand the liquid solidified; m.p. 49–50°. Found: N 7.39; 7.22%. C₁₂H₁₉ON. Calculated: N 7.25%.

The active hydrogen content, by the Tserevitinov-Chugaev method, was 1.04. The hydrochloride had m.p. 75.5–78° (from a mixture of acetone and dry alcohol); it was highly hygroscopic.

4-Dimethylamino-1-phenylbutyl Benzoate Hydrochloride (III) ($R = H$, $Ar = C_6H_5$, $R' = C_6H_5$). A solution of 2.07 g (0.0147 mole) of benzoyl chloride (freshly distilled at 195-197°) in 7 ml of dry benzene was dropped slowly into a solution of 1.00 g (0.00517 mole) of 4-dimethylamino-1-phenyl-1-butanol in 5 ml of dry benzene. On the next day an excess of dry ether was added to the reaction mixture; the precipitate formed was filtered off, washed with dry ether, and crystallized several times from acetone. We obtained 0.90 g (52.2%) of 4-dimethylamino-1-phenylbutyl benzoate hydrochloride, m. p. 136-138°. Found: N 3.99; 3.90; Cl 10.77%, $C_{19}H_{24}O_2NCl$. Calculated: N 4.19; Cl 10.62%.

SUMMARY

1. With a view to a comparative pharmacological investigation some new secondary and tertiary aliphatic-aromatic aminobutanols and some of their esters were synthesized. Their hydrochlorides and methyl methosulfates were also prepared.

2. Considerable difficulties were met in effecting the esterification of tertiary aminobutanols; this contrasts with the behavior of the secondary 4-dimethylamino-1-phenyl-1-butanol, which could be esterified in the usual way.

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PROPERTIES OF 3-MERCAPTO-2,2-DIPHENYLPROPIONIC
 β -THIOLACTONE

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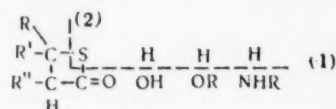
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie, Khimicheskikh Nauk*,

No. 10, pp. 1825-1827, October, 1960

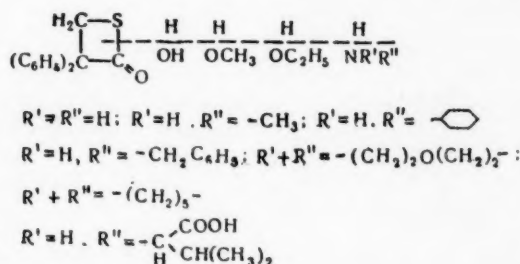
Original article submitted May 20, 1959

Study of the properties of the thiolactones prepared previously has shown that their hydrolysis, alcoholysis, and aminolysis always proceed in the same direction with scission of the sulfur-carbonyl bond [direction (1)] and formation of the corresponding β -mercapto acids or their derivatives [1-4].



It is known that their oxygen analogs undergo cleavage in a way dependent on the reagent, the solvent, or the order of the addition of the reactants, and that this may occur at the oxygen-carbonyl link [direction (1)], or at the O-C link [direction (2)], or in both directions simultaneously; β -substituents favor cleavage mainly in direction (1) and α -substituents favor cleavage in direction (2), with formation of derivatives of β -hydroxy acids or β -substituted carboxylic acids, respectively. Thus, 3-hydroxy-2,2-diphenylpropionic β -lactone (I) is split by alcohols, amines, and salts mainly in direction (2) with formation of β -substituted acids [5].

In this connection it was of interest to prepare 3-mercapto-2,2-diphenylpropionic β -thiolactone (II), the sulfur analog of (I), and investigate its properties. 3-Mercapto-2,2-diphenylpropionic β -thiolactone was prepared by a previously described method from 3-chloro-2,2-diphenylpropionyl chloride [6]. Study of the reactions of 3-mercapto-2,2-diphenylpropionic β -thiolactone showed that, irrespective of the reaction conditions (order of addition of reactants, solvent), hydrolysis and aminolysis go in one direction only with cleavage of the sulfur-carbonyl bond.



Thus, alkaline hydrolysis of (II) leads to 3-mercapto-2,2-diphenylpropionic acid, and aminolysis to the corresponding 3-mercapto-2,2-diphenylpropionamides; in particular, in the case of valine the product is N-(3-mercapto-2,2-diphenylpropionyl)valine. With more prolonged reaction in excess of amine the amides formed are readily oxidized by air to the corresponding disulfides. Sodium alkoxides split the thiolactone with formation of 3-mercapto-2,2-diphenylpropionic esters, which immediately oxidize in air with formation of the corresponding disulfides.

EXPERIMENTAL

N-Benzyl-3-mercapto-2,2-diphenylpropionamide (III). To 0.96 g (0.004 mole) of (II) we added 3.85 ml (0.036 mole) of benzylamine. The reaction was exothermic. The precipitate formed was filtered off on the next day and washed with dilute hydrochloric acid; yield 1.35 g (97%) of (III). After crystallization from acetic acid: m. p. 176-178°. Found: C 75.13; H 5.83; S 8.67%. $C_{22}H_{21}NOS$. Calculated: C 76.07; H 6.05; S 9.22%.

By the use of different solvents (CH_3CN , C_6H_6) and change in the order of addition, we did not succeed in changing the direction in which the cleavage of (II) occurred. (III) was readily oxidized with iodine solution to 3,3'-dithiobis(N-benzyl-2,2-diphenylpropionamide), m. p. 130-133° (from petroleum ether). Found: C 76.22; H 5.81; S 8.34%. $C_{44}H_{40}N_2O_2S_2$. Calculated: C 76.30; H 5.78; S 9.24%. On reduction of the latter with zinc dust in acetic acid (III), m. p. 173-175°, was regenerated in quantitative yield. A mixture test with a known sample of (III) showed no depression of melting point.

1-(3-Mercapto-2,2-diphenylpropionyl)piperidine (IV). To 0.96 g (0.004 mole) of (II) we added 2.4 ml (0.024 mole) of piperidine. The solution was boiled for five hours and then left overnight. On addition of dilute hydrochloric acid a precipitate of (IV) was formed; yield 1.25 g (95%). After crystallization from acetic acid: m. p. 199-200°. Found: C 73.65; H 6.63; S 9.65%. $C_{20}H_{23}NOS$. Calculated: C 73.84; H 7.07; S 9.84%.

4-(3-Mercapto-2,2-diphenylpropionyl)morpholine (V). To 1.1 ml (0.012 mole) of morpholine we added 0.96 g (0.004 mole) of (II). The solution was heated in a water bath for six hours. On addition of water 1.1 g (90%) of (V) separated. After crystallization from petroleum ether: m. p. 167-169°. Found: C 69.65; H 6.58; S 9.29%. $C_{19}H_{21}NO_2S$. Calculated: C 69.72; H 6.42; S 9.78%.

3,3'-Dithiobis(N-cyclohexyl-2,2-diphenylpropionamide) (VI). A solution of 0.96 g (0.004 mole) of (II) in 5 ml of acetonitrile was added to a solution of 1.4 ml (0.012 mole) of cyclohexylamine in 5 ml of acetonitrile, and the mixture was heated in a water bath for six hours. On addition of water 1.3 g (95%) of (VI) separated. After crystallization from petroleum ether: m. p. 116-118°. Calculated: C 74.55; H 7.10; S 9.46%. $C_{42}H_{48}N_2O_2S_2$.

3,3'-Dithiobis(N-methyl-2,2-diphenylpropionamide) (VII). Methylamine was passed for four hours into a solution of 0.96 g (0.004 mole) of (II) in 10 ml of acetonitrile. On the next day the acetonitrile was evaporated off in air, and we obtained 1.05 g (98%) of (VII). After crystallization from aqueous alcohol: m. p. 173-175°. Found: C 71.15; H 5.90; S 11.42%. $C_{32}H_{32}N_2O_2S_2$. Calculated: C 71.11; H 5.92; S 11.85%.

3-Mercapto-2,2-diphenylpropionamide (VIII). Ammonia was passed for three hours into a solution of 0.96 g (0.004 mole) of (II) in 10 ml of acetonitrile. The reaction mixture was warmed, and after 30 minutes it gave a positive reaction for the SH group. After the vaporization of acetonitrile we obtained 1.0 g (97.5%) of (VIII). After crystallization from aqueous alcohol: m. p. 165-167°. Found: C 70.04; H 5.88; S 11.95%. $C_{15}H_{15}NOS$. Calculated: C 70.03; H 5.83; S 12.41%.

N-(3-Mercapto-2,2-diphenylpropionyl)valine (IX). A solution of 0.96 g (0.004 mole) of (II) in 50 ml of alcohol was added to 50 ml of an alcoholic solution of the sodium salt of valine [from 0.7 g (0.006 mole) of valine and 0.24 g (0.006 mole) of sodium hydroxide]. The solution was refluxed for three hours, and alcohol was evaporated off in a stream of nitrogen at low pressure; the dry residue was dissolved in water and acidified. The resulting precipitate (IX) was filtered off, washed with water, and purified by reprecipitation from solution in diethyl ether by petroleum ether; m. p. 93-100° (decomp.); yield 1.2 g (55.6%). Found: C 67.57; H 6.28; S 8.38%. $C_{20}H_{23}NO_3S$. Calculated: C 67.22; H 6.44; S 8.96%.

Dimethyl 3,3'-Dithiobis(2,2-diphenylpropionate) (X). We added 0.96 g (0.004 mole) of (II) to a solution of 0.138 g (0.006 g-atom) of sodium in 5 ml of methanol; after five minutes the mixture gave a positive reaction for the SH group. The solution was heated in a water bath for three hours, and alcohol was evaporated off in the air. The dry residue was extracted with ether. After the evaporation of ether we obtained 1.05 g (96%)

of (X). After crystallization from absolute alcohol: m. p. 120-121°. Found: C 70.38; H 5.18; S 11.81%. $C_{32}H_{30}O_4S_2$. Calculated: C 70.84; H 5.53; S 11.80%. In a similar way we prepared diethyl 3,3'-dithiobis(2,2-diphenylpropionate); yield 88%; m. p. 101-102° (from alcohol). Found: C 72.00; H 6.08; S 11.11%. $C_{34}H_{34}O_4S_2$. Calculated: C 71.92; H 5.94; S 11.22%.

SUMMARY

Under the action of compounds containing a mobile hydrogen atom, 3-mercaptopropionic β -thiolactones undergo cleavage in one direction only with formation of 3-mercaptopropionic acids or their derivatives.

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NEW REACTION OF THIOLS WITH N-SUBSTITUTED FORMAMIDES
AND PHOSPHORYL CHLORIDE

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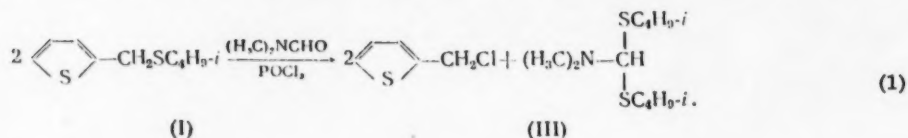
Translated from *Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk*,

No. 10, pp. 1828-1833, October, 1960

Original article submitted May 4, 1959

N-Substituted formamides, especially N-methylformanilide and N,N-dimethylformamide, are now used fairly extensively as formylating agents. By formylating in this way aromatic aldehydes of phenyl ethers and tertiary amines [1, 2] have been prepared together many heterocyclic aldehydes, in particular those derived from thiophene [3].

By the formylation of 2-ethylthiophene with the aid of N,N-dimethylformamide and phosphoryl chloride [4] we obtained a good yield of 5-ethylthio-2-thiophenecarboxaldehyde.* However, when an attempt was made to formylate 2-(isobutylthiomethyl)thiophene (I) and 2-(ethylthiomethyl)thiophene (II) under the same conditions, no products containing the aldehyde function were isolated from the reaction mixture, but 2-(chloromethyl)thiophene was obtained in yields of 61% and 20%, respectively. Also, in the case of 2-(isobutylthiomethyl)thiophene (I) a substance corresponding in analysis to $C_{11}H_{25}NS_2$ was isolated. On the basis of analytical data, and also a study of chemical behavior and absorption spectra,* we concluded that the reaction product $C_{11}H_{25}NS_2$ had the structure 1,1-bis(isobutylthio)-N,N-dimethylmethanamine (III). The reaction may be represented as follows:

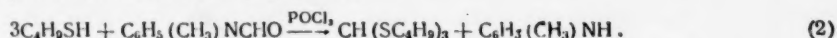


On the other hand, by reaction of N,N-dimethylformamide (1 mole) and 2-methyl-1-propanethiol (2 moles) in presence of phosphoryl chloride (1 mole) in the cold we obtained a 36% yield of the same product (III). By the same method we synthesized the following: 1,1-bisbutylthio-N, N-dimethylmethylaniline (IV) in 41% yield from 1-butanethiol, and N, N-dimethyl-1, 1-bis-*t*-butylthiomethylaniline (V) in 11% yield from 1,1-dimethylethanethiol. It must be pointed out that when condensing agents usually used for the synthesis of mercaptals (dry HCl, ZnCl₂) are employed the reaction does not lead to the formation of substances of this type. Hence, phosphoryl chloride is a specific agent in this new reaction.

Mercaptals of the type (III) are described by us for the first time [5]. They are unpleasantly smelling colorless oils, readily soluble in organic solvents, stable in an alkaline medium, but rapidly hydrolyzed in an acid medium with formation of the thiol and a dimethylamine salt. In an attempt to prepare the picrate of (III) by reaction with an ethereal solution of picric acid the picrate of dimethylamine was obtained. Attempts to prepare the sulfone by the oxidation of (III) were not successful. On treatment with heavy-metal salts (Pb and Hg salts), (III) gave precipitates of mercaptides, from which we were unable to isolate individual compounds.

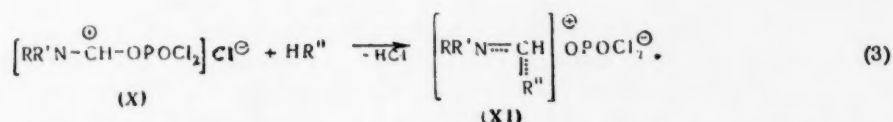
* This will be reported in greater detail in a future communication.

With the object of extending the investigation of the reaction observed between N-substituted formamides and thiols we carried out the reaction with N-methylformanilide instead of N,N-dimethylformamide in the hope of obtaining the corresponding 1,1-bisalkylthio-N-methyl-N-phenylmethylaniline, but the reaction unexpectedly took another course. Thus, in the reaction of N-methylformanilide (1 mole), 2-methyl-1-propanethiol (2 moles), and phosphoryl chloride (1 mole), as the main product we isolated triisobutyl trithioorthoformate (VI) (yield 44 %). Similarly, on reaction of N-methylformanilide with 1-butanethiol we obtained tributyl trithioorthoformate (VII); in addition, from the reaction mixture we isolated N-methylaniline in a yield of 45% on the amount of N-methylformanilide taken. The equation for the reaction is as follows:



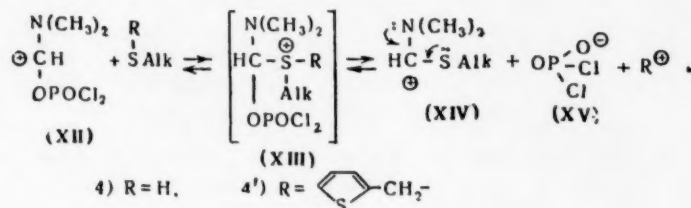
The structures of the trithio ortho esters (VI) and (VII) obtained were confirmed by molecular weight determination and comparison of the melting points of their sulfones (VIII) and (IX) with data in the literature [6]. Reaction according to Equation (2) is a particular case of the reaction described by Holmberg [7, 8] of formic acid and its esters and amides with thiols.

The fact that the reaction of thiols with N,N-dimethylformamide and $POCl_3$ goes under the same conditions and with the same reagents (N,N-dimethylformamide and $POCl_3$) as the reaction of formylation suggests that the mechanisms of these two reactions are similar. The mechanism of formylation with N-substituted amides in presence of $POCl_3$ has been inadequately studied. However, it follows from the work of Mangoni [2] and Smith [9] that reaction proceeds through the stage of a cation of type (XI), which is formed as a result of reaction of the compound being formylated (HR'') and the complex (X) formed by $POCl_3$ with the N-substituted formamide [Equation (3)].

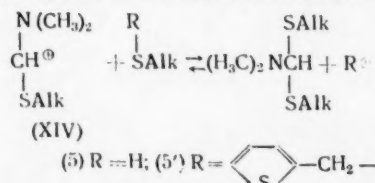


Mangoni [2] and Smith [9] succeeded in isolating and identifying saltlike compounds containing a cation of type (XI), and in showing that on hydrolysis (XI) gives an aldehyde quantitatively.

In the reaction that we have discovered, a strongly electrophilic cation formed from N,N-dimethylformamide and $POCl_3$ (XII) is capable of interaction with the electron pair of a sulfur atom giving the sulfonium complex (XIII); there then occurs the elimination of a cation R^+ and the formation of phosphorodichloridic acid (XV) [Equations (4) and (4')].



The cation (XIV) is analogous in structure to (XI) [in the case of formylation, Equation (5)] and can be stabilized because of some withdrawal of electrons from the neighboring nitrogen and sulfur atoms. Under the conditions of the reaction, (XIV) reacts with another thiol or 2-(alkylthiomethyl)thiophene molecule, and the cation R^+ formed is bound with the aid of (XV) in the case of thiols [Equation (5)], and by reaction with Cl^- ions in the medium gives 2-(chloromethyl)thiophene in the case of sulfides [$R^+ = \text{---}CH_2\text{---}$, Equation (5')].



It is interesting that several cases of the decomposition of benzylthio compounds in an acid medium are known [10], and these are also to be explained by the formation of sulfonium complexes like (XIII) [11].

EXPERIMENTAL

Cleavage of 2-(Isobutylthiomethyl)thiophene (I) and the Preparation of 1,1-Bisisobutylthio-N,N-dimethyl-methylamine (III). Phosphoryl chloride (6.4 ml, 0.06 mole) was added with stirring at from -5° to -3° over a period of 30 minutes to a solution of 11.06 g (0.06 mole) of (I) [b. p. $101-102^{\circ}$ (2 mm); n_D^{20} 1.5442] in 25 ml of N,N-dimethylformamide (DMFA) [b. p. $153-154^{\circ}$ (758 mm); n_D^{20} 1.4302]. The reaction mixture was set aside for 18 hours and then poured at 0° into saturated sodium acetate solution. The mixture was extracted with ether, and the extract was dried with magnesium sulfate. Ether was distilled off, and distillation then gave 5.07 g (61%) of 2-(chloromethyl)thiophene, b. p. $61-64^{\circ}$ (7 mm) and n_D^{20} 1.5630. By the reaction of 2-(chloromethyl)thiophene with sodium methylphenyldithiocarbamate $[C_6H_5(CH_3)NCSSNa]$ in alcohol we obtained the 2-thenyl derivative, m. p. $98-99^{\circ}$. A mixture with a known sample (m. p. $97.5-98.55^{\circ}$) had m. p. $98-99^{\circ}$.

The aqueous layer was neutralized with dry sodium carbonate and extracted with ether. The ether extract was washed with water and dried with anhydrous magnesium sulfate. After removal of ether and distillation of the residue we obtained (III) (1.58 g) as a colorless liquid; b. p. $122.5-123.5^{\circ}$ (5 mm); n_D^{20} 1.4960 and d_4^{20} 0.9399. Found: C 56.22; 56.24; H 10.67; 10.64; S 27.17; 27.87; N 6.11; 6.03%. $C_{11}H_{25}NS_2$. Calculated: C 56.11; H 10.70; S 27.24; N 5.95%. For the compound $(CH_3)_2N-CH(S-CH_2-CH(CH_3)_2)$ the molecular weight, determined by the cryoscopic method, was 233; calculated MR 72.83*, found MR 72.40.

Synthesis of (III) from 2-Methyl-1-propanethiol and DMFA. Phosphoryl chloride (10.5 ml, 0.115 mole) was added with stirring at from -3° to 0° over a period of 45 minutes to a solution of 18 g (0.2 mole) of 2-methyl-1-propanethiol in 7.3 g (0.1 mole) of DMFA. The reaction mixture was set aside for 20 hours and then poured into a saturated solution of sodium carbonate at 0° and extracted with ether. The ether extract was washed with water and dried with anhydrous magnesium sulfate; ether was distilled off, and we then collected 5.6 g of a fraction consisting of almost unchanged pure 2-methyl-1-propanethiol, b. p. $87-88.5^{\circ}$. Vacuum fractionation of the residue gave 8.39 g (35.7% on the amount of thiol taken and 52% on the amount that reacted) of (III) as a colorless liquid, b. p. $122.5-123.5^{\circ}$ (5 mm) and n_D^{20} 1.4943.

The substance (III) is a colorless liquid of unpleasant odor, b. p. $122.5-123.5^{\circ}$ at 5 mm and $127-128^{\circ}$ at 9.5 mm; on distillation at atmospheric pressure it began to decompose at about 180° ; d_4^{20} 0.9399; n_D^{20} 1.4943. The substance is of low solubility in water, but dissolves in most organic solvents; it has basic properties. When kept in the light for one month it decomposes to the extent of about 8-10% with formation of low-boiling products. On being heated with dilute acids it is hydrolyzed with formation of the corresponding dimethylamine salt and the thiol; no other products could be isolated. When an attempt was made to prepare the picrate of (III) by mixing 20 ml of saturated ethereal picric acid and 5 ml of an ethereal solution of 0.2 g of (III), we isolated 0.28 g of a yellow crystalline substance of m. p. $157-158^{\circ}$ (from alcohol), which was identified by means of a mixture melting point test with a known sample of dimethylamine picrate (m. p. 158°).

When attempts were made to prepare derivatives of (III) with utilization of the sulfide function, e. g. by the formation of complexes with heavy-metal salts or by oxidation to the sulfone, it was found that the substance again underwent preliminary hydrolysis in the way indicated above. Thus, on mixing 0.5 g of (III) in 5 ml of absolute alcohol with 2 g of $HgCl_2$ in 10 ml of absolute alcohol we obtained a colorless crystalline product (1.25 g), which contained no nitrogen and decomposed with formation of the thiol. When (III) was oxidized with hydrogen peroxide in acetic acid or with permanganate no individual products could be isolated.

Cleavage of 2-(Ethylthiomethyl)thiophene (II). To a mixture of 12.5 g (0.079 mole) of (II) [b. p. $88-89.5^{\circ}$ (6 mm); n_D^{20} 1.5682] and 30 ml of DMFA dropwise addition was made of 0.83 ml (0.079 mole) of $POCl_3$ at -5° over a period of 25 minutes. After being stirred for two hours with gradual rise of temperature to that of the room, the mixture was left overnight, after which it was poured into saturated sodium acetate solution and extracted with ether. From the dried ether layer we isolated 3.5 g (20%) of 2-(chloromethyl)thiophene, b. p. $63-64^{\circ}$ (9.5 mm)

* The refraction of the C-S bond was taken to be 4.61 [12].

and n_D^{20} 1.5635, which was identified as in the experiment on the cleavage of (I). The aqueous layer was not analyzed.

1,1-Bisbutylthio-N,N-dimethylmethylamine (IV). By the method described for (III), from 36 g (0.4 mole) of 1-butanethiol, 14.6 g (0.2 mole) of DMFA, and 30.6 g (0.2 mole) of POCl_3 we obtained 19.4 g (41%) of (IV); b. p. 134-135° (5 mm); n_D^{20} 1.4979; d_4^{20} 0.9490. Found: C 55.99; 56.19; H 10.49; 10.60; S 27.38; 27.30; N 6.13; 6.09%. $\text{C}_{11}\text{H}_{25}\text{NS}_2$. Calculated: C 56.11; H 10.70; S 27.24; N 5.95%.

N,N-Dimethyl-1,1-bis-t-butylthiomethylamine (V). From 9 g (0.1 mole) of 1,1-dimethylethanethiol, 3.65 g (0.05 mole) of DMFA, and 8.4 g (0.055 mole) of phosphoryl chloride by the method described for (III) we obtained 1.28 g (11%) of (V), b. p. 104-104.2° (6 mm) and n_D^{20} 1.4940. Found: C 55.88; 55.96; H 10.81; 11.19; S 27.27; 27.27; N 6.17; 6.19%. $\text{C}_{11}\text{H}_{25}\text{NS}_2$. Calculated: C 56.11; H 10.70; S 27.24; N 5.95%.

Triisobutyl Trithioorthoformate (VI). Phosphoryl chloride (5.3 ml, 0.06 mole) was gradually mixed with 6.7 g (0.05 mole) of N-methylformanilide and 10.7 ml (0.1 mole) of 2-methyl-1-propanethiol at 0°. The mixture was stirred for one hour, and the cooling bath was then removed; the temperature rose to that of the room, and the mixture was left overnight. The reaction mixture was decomposed at 0° with saturated sodium carbonate solution and was extracted with ether. The ether layer was washed with water and dried with magnesium sulfate; ether was distilled off, and the residue was distilled. We then isolated 4.1 g (44 %) of (VI), b. p. 133-135° (1 mm). (VI) was a yellow odorless mobile liquid; n_D^{20} 1.5102; d_4^{20} 0.9701. Found: C 56.19; 55.96; H 10.02; 9.82; S 33.41; 33.81%. $\text{C}_{13}\text{H}_{28}\text{S}_3$. Calculated: C 55.65; H 10.06; S 34.28%. For the compound $\text{CH}(\text{SC}_4\text{H}_9)_3$ the molecular weight, found by the cryoscopic method, was 265; calculated MR 86.3; found; MR 72.40.

Tributyl Trithioorthoformate (VII). Over the course of 35 minutes 9.15 ml (0.1 mole) of POCl_3 was added to a mixture of 16.1 ml (0.1 mole) of N-methylformanilide and 21.5 ml (0.2 mole) of 1-butanethiol at from -2° to -3°. The clear yellowish solution was left overnight at room temperature; it darkened in color and separated into two layers. After being stirred for two hours at 40-45° the reaction mixture became homogeneous. The thick dark-colored solution was carefully poured at from -5° to 0° into a mixture of a solution of 35 g of KOH in 52 ml of water and 100 ml of ether with stirring and cooling with solid carbon dioxide and acetone. The yellow ether layer was decanted and, without being washed, dried with calcined potassium carbonate. Ether was distilled off, and distillation of the residue gave 12.54 g (69%) of (VII); b. p. 147-148° (1 mm); n_D^{20} 1.5180; d_4^{20} 0.9831. Found: C 56.47; 56.51; H 9.90; 9.85; S 33.36; 33.38%. $\text{C}_{13}\text{H}_{28}\text{S}_3$. Calculated: C 55.65; H 10.06; S 34.28%. For the compound $\text{CH}(\text{SC}_4\text{H}_9)_n$ the molecular weight, determined by the cryoscopic method, was 270; calculated MR 86.3; Found MR 84.0. Also, on treatment of the fraction of b. p. 100-113° (10 mm) with concentrated hydrochloric acid we isolated N-methylaniline hydrochloride (yield 45%), m. p. 121-123°, undepressed by admixture of a known sample of N-methylaniline hydrochloride.

Triisobutylsulfonylmethane (VIII). (VI) (0.5 g) was oxidized with 1.06 g of KMnO_4 in 50 ml of 1 N H_2SO_4 at 30°. The excess of permanganate and the MnO_2 formed were decomposed with bisulfite; the white precipitate formed was filtered off, washed with water, and crystallized from dilute alcohol. The colorless needles obtained (0.11 g) sublimed without melting at about 200°. They were dissolved in warm alkali and reprecipitated by acidification. Found: C 41.80; H 7.49; S 25.14. $\text{C}_{13}\text{H}_{28}\text{O}_6\text{S}_3$. Calculated: C 41.46; H 7.49; S 25.54%.

Tributylsulfonylmethane (IX). On oxidation of 3.38 g of (VII) with 12.7 g of KMnO_4 in dilute sulfuric acid by the method described for the oxidation of (VI) we obtained 0.7 g (15%) of the sulfone, m. p. 233-233.5° (from a mixture of methanol and water). The literature [6] gives m. p. 229-230°. Found: C 41.60; 41.36; H 7.52; 7.45; S 25.40; 25.25%. $\text{C}_{13}\text{H}_{28}\text{O}_6\text{S}_3$. Calculated: C 41.46; H 7.49; S 25.54%.

SUMMARY

1. In the reaction of 2-alkylthiophenes with N,N-dimethylformamide and phosphoryl chloride, cleavage of the sulfides occurs with formation of 2-(chloromethyl)thiophene. In the reaction with 2-isobutylthiophene a substance of a new type was isolated: 1,1-bisisobutylthio-N,N-dimethylmethylamine.

2. With N,N-dimethylformamide in presence of POCl_3 thiols undergo a previously unknown reaction with formation of 1,1-bisalkylthio-N,N-dimethylmethylamines. By this method substances of this type containing different alkyls (butyl, isobutyl, t-butyl) were prepared. N-Methylformanilide reacting with thiols in presence of POCl_3 does not form compounds of the above-described type, but under the same conditions gives trithioorthoformic esters.

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SYNTHESIS OF SOME ALDEHYDES FROM SULFIDES OF
THE THIOPHENE SERIES

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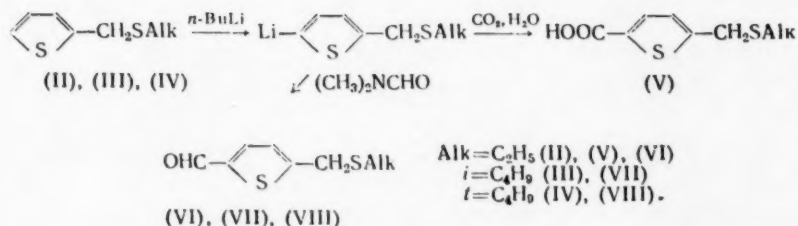
No. 10, pp. 1834-1837, October, 1960

Original article submitted May 4, 1959

By the formylation of 2-ethylthiophene with N,N-dimethylformamide in presence of POCl_3 we obtained a good yield (74%) of 5-ethylthio-2-thiophenecarboxaldehyde (I)*. However, when an attempt was made to formylate 2-(alkylthiomethyl)thiophenes, the reaction went in a different direction [1], and we decided to prepare the aldehydes required by the action of N,N-dimethylformamide on the lithium derivatives of 2-(alkylthiomethyl)thiophenes. Aldehydes of the thiophene series are of interest not only as intermediates in the synthesis of azomethines as ingredients of rubber mixes [2], but also for the preparation of leuco compounds of triarylmethane dyes, which find application in dosimetry in the study of radiation-induced chemical reactions [3].

The replacement of lithium by a formyl group by the action of N,N-dimethylformamide on lithium derivatives of the aromatic series was carried out by Adams and Carlin [4]. This reaction was later applied in the thiophene series by Sicé [5]; in particular he showed that 2-methoxythiophene reacts smoothly with phenyllithium in dry ether with formation of 5-methoxy-2-thienyllithium, which by carbonation is converted in 61% yield into 5-methoxy-2-thiophenecarboxylic acid, and by reaction with N,N-dimethylformamide is converted in 67% yield into 5-methoxy-2-thiophenecarboxaldehyde. It was recently shown by one of the present authors in conjunction with Gol'dfarb and Gorushkina [6] that 2-(ethylthiomethyl)thiophene (II) is metalated by butyllithium in the 5-position with formation of 5-(ethylthiomethyl)-2-thienyllithium, which was converted by carbonation into the carboxylic acid (V) in about 53% yield.

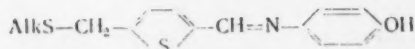
On the basis of this observation we effected the replacement of lithium by the formyl group by the action of N,N-dimethylformamide on 5-(alkylthiomethyl)-2-thienyllithiums^{••} and obtained the 5-(alkylthiomethyl)-2-thiophenecarboxaldehydes (V), (VII), and (VIII). The transformations occurring may be represented as follows:



* While this paper was in the press there appeared a paper [9] on the synthesis of 5-alkylthio-2-thiophenecarboxaldehydes. 5-Ethylthio-2-thiophenecarboxaldehyde was found to have b. p. 82° (0.35 mm) and n_D^{20} 1.6320.

* The 2-(alkylthiomethyl)thiophenes were prepared by the reaction of 2-(chloromethyl)thiophene with thiols [6, 8].

The aldehydes were obtained in 21-34% yield, and in all cases the original sulfides were isolated unchanged in amounts of up to 30%. The reaction was accompanied by much resinification, which may be explained by the instability of the aldehydes, whose molecules contain the methylenethio grouping ($-\text{CH}_2\text{S}-$). The relatively low yields of aldehydes are explained by the formation of resinification products. The aldehydes were characterized by their semicarbazones and dinitrophenylhydrazones. In addition, azomethines were prepared from them with *p*-aminophenol, namely



in which Alk is ethyl (IX) or isobutyl (X). 5-Ethylthio-2-thiophenecarboxaldehyde (I) was also converted into its azomethine with *p*-aminophenol (XI).

EXPERIMENTAL

5-Ethylthio-2-thiophenecarboxaldehyde (I). Dropwise addition was made of 7.8 ml (0.085 mole) of POCl_3 over a period of 15 minutes to a mixture of 30 ml of *N,N*-dimethylformamide (DMFA) and 9.8 g (0.068 mole) of 2-ethylthiophene [b. p. 89-90° (22 mm); n_D^{20} 1.5708] [7] at from -5° to 0°, after which stirring was continued for one hour, in the course of which the temperature rose to that of the room. The reaction mixture was left for two days and then stirred into a sodium acetate solution. The mixture was extracted with ether, and the ether layer was washed with 1 N HCl, with bicarbonate solution, and with water; it was then dried with anhydrous magnesium sulfate, and ether was distilled off. We obtained 7.71 g (74%) of the aldehyde (I), b. p. 114.5-116° (1 mm). Found: C 48.96; 48.99; H 4.78; 4.84; S 37.38; 37.43%. $\text{C}_7\text{H}_8\text{OS}_2$. Calculated: C 48.80; H 4.68; S 37.23%. Semicarbazone, m. p. 179-180° (from alcohol). Found: N 17.97; 18.25%. $\text{C}_8\text{H}_{11}\text{N}_3\text{OS}_2$. Calculated: N 18.35%.

2-t-Butylthiophene (IV). A mixture of a solution of 3.4 g (0.15 g-atom) of sodium in 60 ml of absolute alcohol, 13.5 g (0.15 mole) of 1,1-dimethylethanethiol (b. p. 63-65°), and 13.3 g (0.1 mole) of 2-(chloromethyl)thiophene [b. p. 77-78° (18 mm), n_D^{20} 1.5630] was heated for three hours at 40-45° with stirring; the reaction mixture was poured into water, and the precipitated oil was extracted with ether. The ether layer was washed with water, dried with anhydrous magnesium sulfate, and distilled. We obtained 14.5 g (78%) of the sulfide (IV), b. p. 102-103.5° (6 mm) and n_D^{21} 1.5435. Found: C 58.38; 58.22; H 7.46; 7.38; S 33.81; 34.17%. $\text{C}_9\text{H}_{11}\text{S}_2$. Calculated: C 58.00; H 7.57; S 34.40%.

5-(Ethylthiomethyl)-2-thiophenecarboxaldehyde (VI). Into a flask filled with nitrogen we poured 51 ml of an ethereal solution containing 3.2 g (0.05 mole) of butyllithium, and at from -5° to 0° over a period of ten minutes we added a solution of 7.9 g (0.05 mole) of 2-(ethylthiomethyl)thiophene (II) [b. p. 85-86° (4.5 mm); n_D^{20} 1.5670] in 50 ml of dry ether. After being stirred for two hours at 0° the reaction mixture was poured into a flask filled with nitrogen and containing 4.0 g (0.055 mole) of DMFA in 30 ml of dry ether cooled to -10°. In the course of stirring for three hours the temperature was raised to 0°, and the mixture was then left overnight. The reaction mixture was poured onto 200 g of ice, the ether layer was separated, the aqueous layer was extracted with ether, and the combined ether extract was washed twice with water and dried with anhydrous magnesium sulfate. Ether was distilled off, and the residue, which contained much resin, was distilled. We then isolated 0.3 g (4%) of unchanged (II), b. p. 84-88° and n_D^{20} 1.5662, and 3.15 g (34%) of (VI), b. p. 126-127° (0.6 mm) and n_D^{20} 1.6032. Found: C 51.81; 52.09; H 5.42; 5.47; S 34.30; 34.57%. $\text{C}_8\text{H}_{10}\text{OS}_2$. Calculated: C 51.57; H 5.41; S 34.42%. Semicarbazone, m. p. 192-193° (from alcohol). Found: N 17.19; 17.09%. $\text{C}_9\text{H}_{13}\text{N}_3\text{OS}_2$. Calculated: N 17.27%. *p*-Nitrophenylhydrazone, m. p. 158-159° (from alcohol). Found: N 13.13; 13.05%. $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_2\text{S}_2$. Calculated: N 13.10%.

5-(Isobutylthiomethyl)-2-thiophenecarboxaldehyde (VII). From 37.2 g (0.2 mole) of 2-(isobutylthiomethyl)thiophene (III) [b. p. 100.5-102° (2 mm); n_D^{20} 1.5435] [8], 12.8 g (0.2 mole) of butyllithium in 280 ml of ether, and 16.1 g (0.22 mole) of DMFA in 50 ml of dry ether, by the method described for (VI), we isolated 11.2 g (30% of the amount taken for reaction) of unchanged sulfide (III), b. p. 98-103° (2 mm) and n_D^{20} 1.5418, and obtained 9.1 g of (VII) (21%, or 30% of the sulfide that reacted), b. p. 132.5-133° (0.8 mm) and n_D^{20} 1.5764. Found: C 56.54; 56.60; H 6.65; 6.73; S 29.09; 29.29%. $\text{C}_{10}\text{H}_{14}\text{OS}_2$. Calculated: C 56.03; H 6.58; S 29.92%. Semicarbazone,

* Despite numerous attempts to purify the aldehyde by fractionation we did not obtain a stable substance: after distillation the aldehyde turns red very rapidly. This apparently explains discrepancies in the analysis.

m. p. 200-200.5° (from mixture of alcohol and water). Found: N 15.67; 15.64%. $C_{11}H_{17}N_3OS_2$. Calculated: N 15.50%. 2,4-Dinitrophenylhydrazones, m. p. 193-194° (from CCl_4). Found: N 14.02; 13.97%. $C_{16}H_{18}N_4O_4S_2$. Calculated: N 14.22%.

5-(t-Butylthiomethyl)-2-thiophenecarboxaldehyde (VIII). From 14.4 g (0.076 mole) of 2-(t-butylthio-methyl)thiophene (IV), 4.9 g (0.076 mole) of butyllithium in 110 ml of ether, and 7.0 g (0.096 mole) of DMFA in 30 ml of dry ether by the method described for (VI) we isolated 0.9 g of unchanged sulfide (IV) (b. p. 90-96° at 2 mm; n_D^{20} 1.5388) and obtained 4.8 g [28%, or 30.5% on the amount of (IV) that reacted] of (VIII), b. p. 123.5-125° (0.2 mm) and n_D^{20} 1.5751. Found: C 55.97; 56.09; H 6.53; 6.53; S 29.62; 29.78%. $C_{10}H_{14}OS_2$. Calculated: C 56.03; H 6.58; S 29.92%. Semicarbazone, m. p. 207-207.5° (from mixture of alcohol and water). Found: N 15.78; 15.82%. $C_{11}H_{17}N_3OS_2$. Calculated: N 15.50%.

p-[(5-Ethylthiomethyl-2-thenylidene)amino]phenol (IX). A mixture of 1.25 g (0.007 mole) of (VI) and 0.75 g (0.007 mole) of p-aminophenol was heated in 30 ml of alcohol with the addition of a few drops of glacial acetic acid for three hours, and the crystals that separated with cooling were filtered off and recrystallized from alcohol. We obtained 2.0 g (72%) of (IX), m. p. 132-133°. Found: N 5.24; 5.25%. $C_{14}H_{15}NOS_2$. Calculated: N 5.05%.

p-[(5-Isobutylthiomethyl-2-thenylidene)amino]phenol (X). By the method described for (IX), from 2.2 g (0.01 mole) of the aldehyde (VII) and 1.1 g (0.01 mole) of p-aminophenol we obtained 2.4 g (77%) of (X), m. p. 130-131° (from methanol). Found: N 4.51; 4.61%. $C_{16}H_{19}NOS_2$. Calculated: N 4.58%.

p-[(5-Ethylthio-2-thenylidene)amino]phenol (XI). From 1.4 g (0.008 mole) of (I) and 0.8 g (0.008 mole) of p-aminophenol by the method described for (IX) we obtained 2.05 g (92%) of (XI), m. p. 162-163°. Found: N 5.70; 5.57%. $C_{13}H_{13}NOS_2$. Calculated: N 5.32%.

SUMMARY

1. By the action of N,N-dimethylformamide on lithium derivatives of 2-(alkylthiomethylthiophenes the following aldehydes of the thiophene series were synthesized: 5-(ethylthiomethyl)-, 5-(isobutylthiomethyl)-, and 5-(t-butylthiomethyl)-2-thiophenecarboxaldehydes. By reaction of 2-ethylthiothiophene with N,N-dimethylformamide in presence of phosphoryl chloride, 5-ethylthio-2-thiophenecarboxaldehyde was synthesized.

2. From the above aldehydes and p-aminophenol new azomethines were prepared: p-[(5-ethylthiomethyl-2-thenylidene)amino]phenol, p-[(5-isobutylthiomethyl-2-thenylidene)amino]phenol, and p-[(5-ethylthio-2-thenylidene)amino]phenol.

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REACTIONS OF HYDROCARBONS IN METAL MELTS

COMMUNICATION 1. ACCELERATION AND RETARDATION OF THE CRACKING OF HEPTANE IN MOLTEN ALUMINUM AND SODIUM

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 10, pp. 1838-1843, October, 1960
Original article submitted May 23, 1959

Many metals in the finely divided or molten condition react with hydrocarbons and hydrocarbon radicals with formation of organometallic compounds and carbides and also have a catalytic effect on the transformations of the hydrocarbons. These reactions have recently attracted particularly great interest in connection with the discovery of the direct synthesis of alkylaluminums from the metal, ethylene, and hydrogen. Below (Fig. 1) we give a scheme of various reactions occurring between metals and hydrocarbons. Also, technological processes are known for the preparation of ethylene by the pyrolysis of petroleum fractions in molten lead, for the preparation of biphenyl from benzene, etc. [1-12].

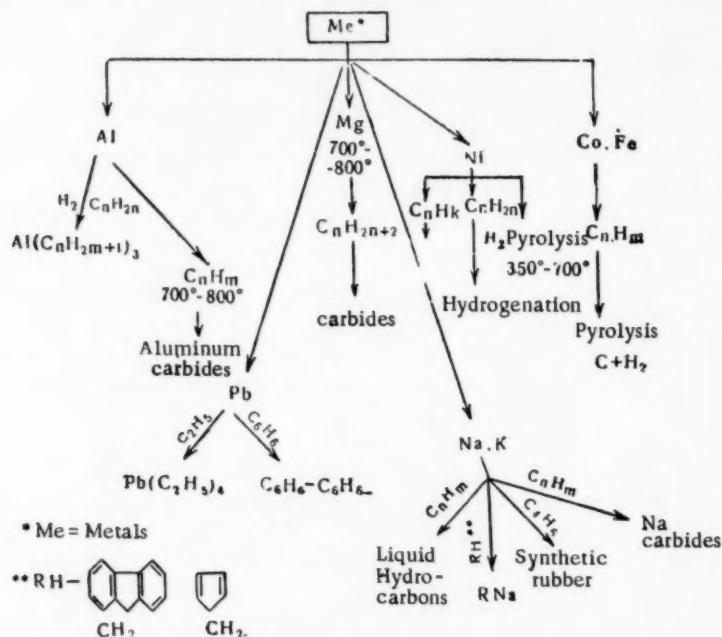


Fig. 1. Scheme of various reactions occurring in the interaction between metals and hydrocarbons.

In view of the above considerations it was of great interest to make a detailed study of the reaction of hydrocarbons with various metals in the most reactive, i. e., molten, state at various temperatures, including high temperatures under conditions for the formation of free radicals, which readily react. The authors carried out an investigation of the high-temperature transformations of heptane in molten sodium and molten aluminum. A continuously operating apparatus was set up (Fig. 2). The apparatus included purification columns filled with reagents for the purification and drying of nitrogen and gaseous hydrocarbons from oxygen and water vapor, a pump, a vaporizer reactor provided with electrical heating, a condenser, and a receiver. The reactor was a 500-ml hollow stainless-steel cylinder. The metal was placed in the reactor, and through a layer of the molten metal (height of layer 150 mm) hydrocarbon vapor was bubbled continuously. The reaction products passed through the condenser to the receiver, where the liquid products were retained, and the gaseous products passed through a meter to the atmosphere. During the experiment a test sample of the gas was taken for analysis. Since molten aluminum dissolves steel, in the work with aluminum the reactor, the thermocouple pocket, and entry tube were protected with graphite.

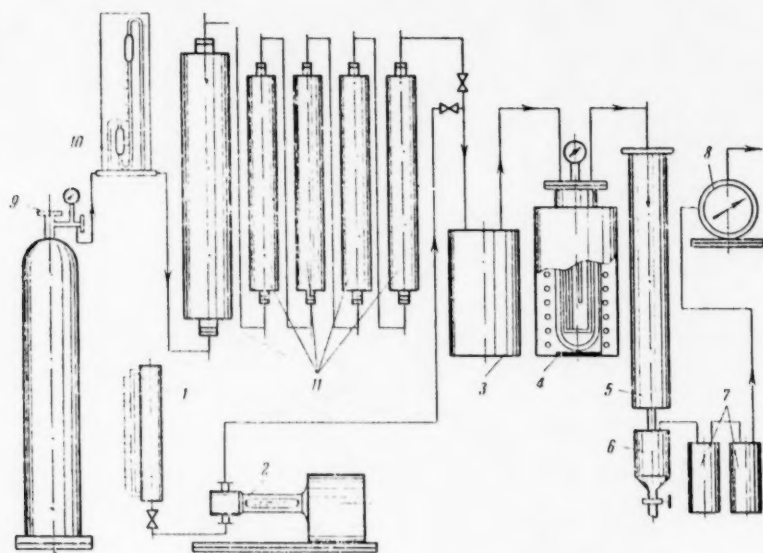


Fig. 2. Diagram of apparatus: 1) reservoir for raw material; 2) pump; 3) vaporizer; 4) reactor; 5) condenser; 6) receiver; 7) strongly cooled vessels; 8) gas meter; 9) gas cylinder; 10) flowmeter; 11) purification and drying columns.

Characteristics of Starting Materials. Technical aluminum in ingots; 99.5-99.7% aluminum; m. p. 659.8°. Sodium; density 0.971; m. p. 97.7°; b. p. 880.9°. Heptane was purified by distillation over sodium; b. p. 98°; density at 20° 0.6803; refractive index n_D^{20} 1.3960; unsaturated compounds absent.

Table 1 gives the results of comparative experiments on the pyrolysis of heptane in molten aluminum and molten sodium, and also in absence of metal. The time of contact of hydrocarbon vapor with metal at 700-800° was about 0.5 second.

The most profound transformations of heptane are observed in contact with aluminum, and here the conversion of heptane increases with rise in temperature and time in the reaction zone: the conversion is 65.3% at 700° and approaches 100% at 800°. Even at 800°, however, heptane undergoes only slight changes in contact with sodium: the conversion is about 5%. Sodium has a retarding effect on the pyrolysis of heptane, for in absence of metal (in an unfilled reactor) the conversion of heptane at 800° attains 57.5% (see Figures 3 and 4 and Table 1).

TABLE 1

Conditions and Material Balance of Pyrolysis of Heptane in Molten Metals

Temperature °C	Rate of feed of raw material (ml/hr)	Yield (% by wt.)			Conversion (% by wt.)
		Gas	Liquid	Condensation products + losses	
Sodium					
Gas formation and cracking absent •					
200	68				
300	57	0,1	94,2*		0,1
450	71	1,8	80,3*		1,8
500	51	2,5	75,1*		2,5
600	60	5,6	74,2*		5,6
700	83	6,8	74,0*		6,8
750	85	5,5	91,1*		5,5
800	108	5,4	83,8*		5,4
Aluminum					
700	100	50,7	43,7	5,6	65,3
750	100	78,0	9,7	12,3	97,1
800	109	72,5	12,3	15,2	99,5
700	112	27,5	67,5	5,0	49,0
700	66	36,9	58,7	4,4	71,0
800	140	45,7	44,6	9,7	78,2
800	86	77,3	14,6	8,7	100,0
800	69	71,0	6,4	22,6	100,0
Unfilled reactor					
700	107	12,2	86,6	1,2	29,0
800	104	27,9	64,3	7,8	57,5

*Unchanged heptane.

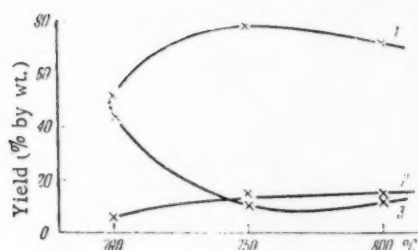


Fig. 3. Temperature dependence of yield of pyrolysis products of heptane obtained in an aluminum melt: 1) gas; 2) condensation products; 3) liquid products.

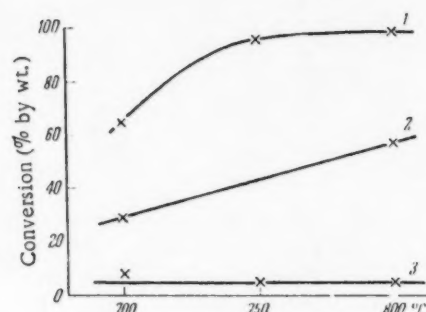


Fig. 4. Temperature dependence of conversion in pyrolysis of heptane (gas + liquid products + condensation products) in: 1) molten aluminum; 2) an unfilled reactor; 3) molten sodium.

The difference in character between the transformations of heptane in contact with sodium and with aluminum is indicated also by the composition of the gas (Tables 2 and 3). Whereas the composition of the gas obtained in the pyrolysis of heptane in contact with aluminum differs little from that of the gas obtained by thermal pyrolysis (higher yields, but the same range of hydrocarbons), the gas obtained in contact with sodium differs considerably in composition: there is almost complete absence of unsaturated hydrocarbons, and the bulk of the gas is hydrogen.

TABLE 2

Composition of Gas from the Pyrolysis of Heptane in Molten Metals

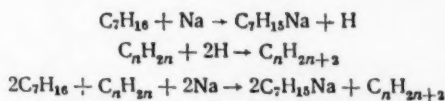
Temperature °C	Composition of gas (% by volume)			Wt. of one liter of gas (g)
	$C_n H_{2n}$	H_2	$C_n H_{2n+2}$	
Sodium				
	Gas formation does not occur			
200		75,0	22,8	0,45
300	2,2	77,0	20,0	0,45
450	3,0	70,3	18,9	0,57
500	10,8	78,5	14,2	0,30
600	7,3	83,5	14,0	0,34
700	2,5	84,6	14,4	0,252
750	1,0	83,6	15,6	0,27
800	0,5			
Aluminum				
700	50,2	15,3	34,5	1,17
750	42,3	24,2	33,5	0,97
800	36,2	30,5	33,3	0,85
Unfilled reactor				
700	40,4	12,2	47,4	1,06
800	44,0	22,0	34,0	0,993

TABLE 3

Individual-hydrocarbon Composition of the Gas from the Pyrolysis of Heptane in Molten Metals

Gas component	Al		Na	Gas component	Al		Na
	700°	800°	700°		700°	800°	700°
percent by volume				percent by volume			
Hydrogen	16,15	31,3	83,5	2-Methylpropene + 1-butene	1,84	1,83	
Methane	26,50	30,6		cis- and trans-2-Butene	0,58	0,14	
Ethane	8,95	5,8		cis- and trans-2-Butene + C_4H_6	0,90	0,51	
Ethylene	31,15	21,91		Isopentane + 3-methyl-1-butene	0,48	0,41	
Propane	0,48	0,26		Pentane	0,15	0,61	
Propene	11,15	6,5		1-Pentene	1,11		
Isobutane	0,34	—					
Butane	0,24	0,13					

In the pyrolysis of heptane in presence of sodium a retardation of cracking is observed. The gas contains 75-85% by volume of hydrogen and only a very small amount of olefins. This may be explained by the following interconnected group of reactions:



At 300-800° in the initial stage there occurs the formation of organosodium compounds with liberation of hydrogen, which at the moment of its formation adds to olefins and so retards cracking, which is a chain process promoted by olefins.

TABLE 4

Characteristics of Liquid Products of the Pyrolysis of Heptane in Molten Metals

Temp. °C	Mixture of liquid reaction products						Chem. comp. of reaction products*		
	Fractional comp.			Sp. gr. d_{44}^{20}	n_D^{20}	Iodine value	Sulfonat- ables (% by wt.)	Unsat. hydro- carbons	aromatic hydro- carbons
	up to 98°	98°	>98°						
—	Original heptane			0,6803	Sodium 1,3960	0	—	—	—
200	—	100,0	—	0,6808	1,3960	0	—	—	—
300	—	100,0	—	0,6870	1,3960	0	—	—	—
450	—	100,0	—	0,6811	1,3950	0	—	—	—
500	—	100,0	—	0,6825	1,3960	0	—	—	—
600	—	100,0	—	0,7000	1,4050	3,1	—	—	—
700	—	100,0	—	0,6846	1,3960	1,3	—	—	—
750	—	100,0	—	0,6820	1,3950	0,8	—	—	—
800	—	100,0	—	0,6803	1,3980	1,2	—	—	—
Aluminum									
700	15,4	80,0	4,6	0,7031	1,4110	31,8	20,7	60,4	39,6
750	16,0	70,0	14,0	0,8535	1,5470	55,8	70,0	31,4	68,6
800	43	0	57,0	0,9708	1,6480	65,8	95,8	27,2	72,8
Unfilled reactor									
700	1,3	85,0	13,7	0,6863	1,3985	15,0	10,0	40,0	60,0
800	5,3	82,4	12,3	0,6882	1,3985	12,0	17,6	18,8	81,2

* The chemical composition is given for the liquid reaction products without unchanged heptane.

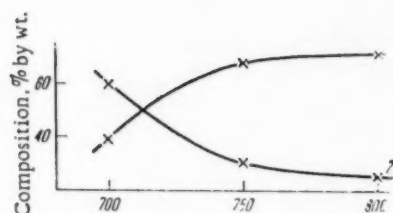


Fig. 5. Temperature dependence of the chemical composition of the products of the pyrolysis of heptane in molten aluminum: 1) aromatic hydrocarbons; 2) unsaturated hydrocarbons.

No liquid reaction products were found in the pyrolysis of heptane in molten sodium. The heptane leaving the reactor was unchanged (Table 4).

In contact with aluminum heptane gives liquid reaction products characteristic for far-reaching pyrolysis: unsaturated and aromatic hydrocarbons at 700° and a highly aromaticized product at 800° (Table 4 and Fig. 5). In both cases, with aluminum and with sodium, condensation products including carbides are formed.

SUMMARY

1. It was found for the first time that the pyrogenetic transformations of heptane in molten aluminum and in molten sodium proceed in a selective manner which depends on the identity of the metal.
2. The extent of the thermal decomposition of heptane is increased by the use of aluminum: in thermal pyrolysis the conversion of heptane (57%) is less than the conversion in contact with aluminum (99%) by nearly one-half.
3. Sodium has a powerful retardant action on the thermal decomposition of heptane: the conversion of heptane in contact with sodium attains only 5-6% at 600-800°.
4. The gas obtained by the pyrolysis of heptane in molten aluminum contains 40-44% of olefins and 12.22% of hydrogen. On the other hand, the pyrolysis of heptane in molten sodium is accompanied by the formation of gas containing 75-85% of hydrogen without any appreciable amount of olefins.

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CATALYTIC TRANSFORMATIONS OF CYCLOHEXANE, METHYL -
CYCLOHEXANE, AND HEXANE OVER A PALLADIUM-ALUMINA
CATALYST UNDER CONDITIONS OF HIGH TEMPERATURE AND
HIGH PRESSURE OF HYDROGEN

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 10, pp. 1844-1847, October, 1960
Original article submitted

In previous investigations [1-4] we studied the catalytic properties of 0.5% palladium-alumina catalysts under the conditions for the reforming of the narrow gasoline fractions of Il'skaya-Khadyzhin and Volga-Urals petroleums. The application of the combination method of analysis [5] both to the original gasoline fraction and to the catalyzates obtained permitted us to determine the extents to which individual classes of hydrocarbons participated in the formation of aromatic compounds. To confirm the results that we obtained in the reforming of a gasoline fraction [3] we considered it to be of interest to study the transformations of individual C_6 hydrocarbons present in gasoline fractions, namely cyclohexane, methylcyclopentane, and hexane.

EXPERIMENTAL

As catalyst we used palladized alumina containing 0.5% of palladium and treated with hydrofluoric acid and hydrogen sulfide. We have previously described in detail the preparation of such a catalyst [3]. Under the conditions for the reforming of a gasoline fraction this catalyst had high activity and maximum stability.

The hexane taken for investigation had: b. p. 68.5° (754 mm); n_D^{20} 1.3750; and d_4^{20} 0.6599. The methylcyclopentane was prepared by the dehydration and isomerization of cyclohexanol over alumina at 450° and $v = 0.3 \text{ hr}^{-1}$ with subsequent hydrogenation of the mixture of unsaturated hydrocarbons in an autoclave in presence of Raney nickel and fractionation through a column of 80-plate efficiency. The resulting methylcyclopentane had b. p. 71.8° (752 mm), n_D^{20} 1.4100, and d_4^{20} 0.7487. The cyclohexane used had b. p. 80.8° (756 mm); n_D^{20} 1.4262, and d_4^{20} 0.7782.

The experiments were carried out in a flow-type apparatus [6] at $475\text{-}480^\circ$ in presence of hydrogen at 20 atm with a space velocity of feed of hydrocarbons of 1.0 hr^{-1} and a molar ratio of hydrogen to hydrocarbons of 5 : 1. The reactor was charged with 30 ml of reduced catalyst.

The properties of the liquid catalyzates were characterized by determinations of specific gravity, refractive index, and content of aromatic hydrocarbons which was determined by the sulfuric acid method. The aromatic hydrocarbons were separated by means of chromatographic adsorption on silica gel. Both the aromatic and the naphthene-paraffin hydrocarbons were then fractionated through columns of 40-plate efficiency and investigated with the aid of Raman spectra. The gaseous catalysis products were analyzed in a VTI apparatus and contained 98.5-99% of pure hydrogen.

Cyclohexane. By the catalytic treatment of cyclohexane under the conditions stated we obtained a catalyzate having n_D^{20} 1.4562, d_4^{20} 0.8134, and an aromatics content of 50%. The aromatic part of the catalyzate had b. p. 80° , n_D^{20} 1.5000, and d_4^{20} 0.8785, which corresponds to benzene. The properties of the naphthene-paraffin part of the catalyzate are given in Table 1.

TABLE 1

Fractional Composition and Properties of Naphthene-Paraffin Part of Cyclohexane Catalyzate*

Fraction	Boiling range (°C)	a-mount (g)	Yield of fraction, % by wt.		n_D^{20}	d_4^{20}	Hydrocarbon composition
			on naphthene-paraffin part	on original cyclohexane			
I	43,0—50,5	1,3	3,7	1,8	1,3695	0,6496	2,2-Dimethylbutane present
II	50,5—60,5	1,5	4,1	2,1	1,3890	0,6913	Hexane 90%, methylcyclopentane 10%
III	60,5—68,0	16,6	46,9	23,4	1,4140	0,7518	Methylcyclopentane 75%, cyclohexane 25%
IV	68,0—71,8	7,6	21,5	10,7	1,4150	0,7577	Methylcyclopentane 70%, cyclohexane 30%
V	71,8—80,0	2,3	6,6	3,3	1,4235	0,7702	Cyclohexane 95%, methylcyclopentane 5%
	80,0—89,0	2,3	6,6	3,3	1,4260		
	Residue	1,2	3,3	1,7			
	Losses						

TABLE 2

Fractional Composition and Properties of the Naphthene-Paraffin Part of the Methylcyclopentane Catalyzate**

Fraction	Boiling range (°C)	a-mount (g)	Yield of fraction, % by wt.		properties of fraction		Hydrocarbon composition
			on naphthene-paraffin part	on original methylcyclopentane	n_D^{20}	d_4^{20}	
I	31,5—45,0	2,2	3,8	2,5	1,3620	0,6341	Pentane present
II	45,0—61,0	2,5	4,3	2,9	1,3760	0,6613	2,3-Dimethylbutane detected
III	61,0—64,0	2,6	4,5	3,0	1,3770	0,6655	Mainly 3-methylpentane
IV	64,0—70,0	3,5	6,0	4,0	1,3880	0,6920	Hexane 35%, methylcyclopentane 65%
V	70,0—72,0	41,6	72,2	48,4	1,4080	0,7436	Mainly methylcyclopentane
VI	Residue	3,8	6,5	4,4	1,4175		Methylcyclopentane 55%, cyclohexane 45%
	Losses	1,6	2,7	1,8			

It follows from Table 1 that the naphthene-paraffin part of the catalyzate contained C_6 paraffins (about 8%) and considerable amounts of cyclopentanes (about 43%). Hence, cyclohexane undergoes the following changes over a palladium-alumina catalyst: dehydrogenation to benzene (about 50%), isomerization with ring contraction (about 30%), and a small amount of hydrogenolysis with formation of paraffins (about 4%) which appear to result through the intermediate stage of ring contraction with formation of cyclopentanes.

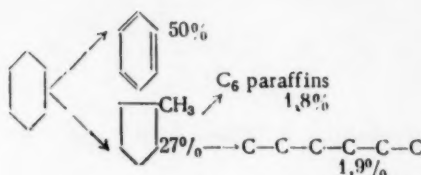
* For fractionation we took 47.0 ml having n_D^{20} 1.4140, and d_4^{20} 0.7506.** For fractionation we took 79.0 ml having n_D^{20} 1.4040, and d_4^{20} 0.7316.

Hexane. In the transformations of hexane over a palladium-alumina catalyst we obtained a catalyzate having n_D^{20} 1.3885, d_4^{20} 0.6870, and an aromatics content of 9.5%. Apart from unchanged hexane, the paraffin-naphthene part of the catalyzate contained branched hydrocarbons (about 5%).

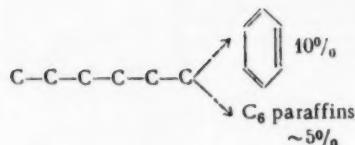
Methylcyclopentane. The combined catalyzates, containing 33% of aromatic hydrocarbons and having n_D^{20} 1.4445 and d_4^{20} 0.7911, were resolved chromatographically on silica gel. The aromatic part of the catalyzate had the constants of benzene: n_D^{20} 1.5010 and d_4^{20} 0.8785. The results of the fractionation of the paraffin-naphthene part of the catalyzate are presented in Table 2. It follows from Table 2 that, apart from unchanged methylcyclopentane, the catalyzate contains about 11% of hydrogenolysis products, namely 2,3-dimethylbutane, 3-methylpentane, and hexane, and also a hydrocracking product, pentane (about 3.8%); a very small amount (about 1.2%) of cyclohexane was found in the residue. Hence, methylcyclopentane undergoes isomerization into cyclohexane and subsequent dehydrogenation to benzene, hydrogenolysis with formation of 2,3-dimethylbutane, 3-methylpentane, and hexane, and hydrocracking with formation of pentane.

On the basis of the investigation of the catalysis products the transformations of the hydrocarbons studied can be represented by the following schemes:

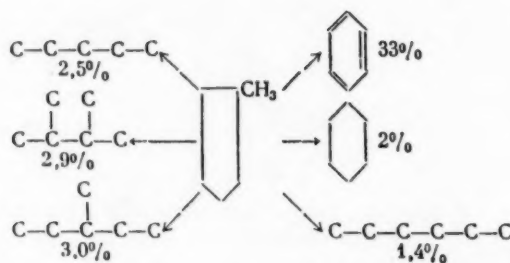
I. Cyclohexane



II. Hexane



III. Methylcyclopentane



SUMMARY

1. A study was made of the transformation of cyclohexane, methylcyclopentane, and hexane over a 0.5% palladium-alumina catalyst under optimum reforming conditions for gasoline fractions of Volga-Urals petroleum (480°, 20 atm, H_2 : hydrocarbon = 5, $v = 1.0$ hr⁻¹).

2. Benzene was the main product and was formed by the dehydrogenation of cyclohexane, the dehydroisomerization of methylcyclopentane, and in small amount by the dehydrocyclization of hexane.

3. Over the palladium-alumina catalyst there occurred also isomerization of hexane and cyclohexane, slight hydrogenolysis of methylcyclopentane, and extremely slight (1.5-2%) hydrocracking of the latter.

4. By this investigation of the transformations of individual C_6 hydrocarbons the mechanism of the formation of aromatic hydrocarbons in the reforming of gasoline fractions of Volga-Urals petroleum was confirmed.

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SYNTHESIS AND PROPERTIES OF HYDROCARBONS OF MIXED STRUCTURE AND HIGH MOLECULAR WEIGHT

COMMUNICATION 1. SYNTHESIS OF C₂₄ HYDROCARBONS

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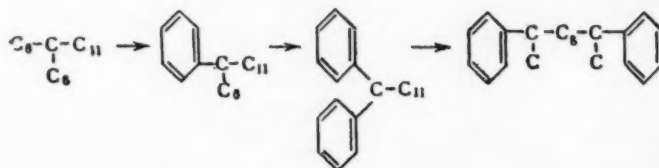
No. 10, pp. 1848-1857, October, 1960

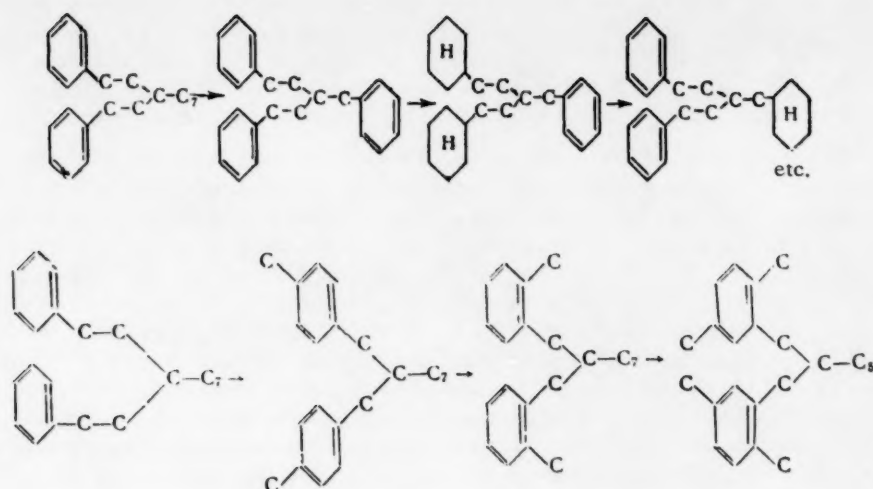
Original article submitted May 6, 1959

Hydrocarbons present in oily petroleum fractions usually have mixed structures, i. e. their molecules are made up of structural units of different classes: aromatic, cycloalkane, and paraffin. A little information has accumulated on the properties and reactions of synthetic hydrocarbons of this type with more than twenty carbon atoms in the molecule. However, the detailed investigation of the high-molecular-weight part of petroleum is being held back by the absence of standard synthetic hydrocarbons, the study of whose properties could serve as a basis for the development of reliable physicochemical methods of analysis of the corresponding hydrocarbon mixtures. We have therefore undertaken synthetic investigations with the object of obtaining a series of individual hydrocarbons, which can to a certain extent serve as models for hydrocarbons present in high-boiling petroleum fractions.

The present communication is devoted to the synthesis and properties of twenty-three previously undescribed hydrocarbons of mixed structure containing twenty-four carbon atoms in the molecule. The general plan of the synthesis was such that on the basis of the behaviour of a large group of hydrocarbons it was possible to follow quantitatively the effects of individual structural units on the properties of the hydrocarbon molecule as a whole [1]. Work having similar objects (admittedly for hydrocarbons of a different molecular weight) was carried out some years ago by R. Shiesler et al. [2]. However, we have extended the limits of the variation of the structural elements present in the hydrocarbons synthesized, and moreover the number of physicochemical methods used for the investigation of the hydrocarbons obtained has greatly increased.

In the present work we resolved the following fundamental questions concerning the part played by various structural changes on the properties of the molecule as a whole: 1) effect of the degree of cyclization on the hydrocarbon molecule (over-all effect, i. e. the effect of both aromatic and cycloalkane rings); 2) effect of the relative dispositions of several rings in the paraffin chain of the molecule; 3) effect of the degree of substitution of the aromatic or cycloalkane rings in the molecule. Diagrammatically these structural changes may be represented as follows:





In an analogous way a study was made of the effect of cycloalkane rings on the properties of the molecule as a whole.

EXPERIMENTAL

The hydrocarbons were synthesized with the aid of the Grignard reaction. Guided by the view that the purity of the hydrocarbons obtained is determined mainly by correct planning of the course of the synthesis and the purity of the reactants, we selected our reactants so that possible by-products and unchanged reactants differed markedly in boiling point from the desired products. One of the most difficult and crucial stages of the synthesis of the hydrocarbons by the Grignard reaction was that of the dehydration of alcohols. The use of reagents of an acid type such as are usually employed for the dehydration of high-boiling alcohols often leads to the formation of impurities in the hydrocarbons obtained. We therefore used vapor-phase dehydration of alcohols in a flow system with pure alumina as catalyst, i. e. we used the same method for the dehydration of alcohols as has been used successfully in the well-known investigations of the American Petroleum Institute for the preparation of highly pure C_6-C_{10} hydrocarbons [3]. However, in our case, because of the high boiling points of the alcohols, it was necessary to carry out the dehydration in a vacuum of 3-4 mm residual pressure. It must be particularly emphasized that the use of a vacuum facilitates the dehydration considerably. The preliminary purification of the hydrocarbons obtained was carried out by fractionation through a special vacuum column with a glass filling and having an efficiency of 16 theoretical plates. The use of an internal tube of large diameter (20 mm) in the column ensured a very small fall in pressure between the top and the bottom of the column, which prevented overheating of the liquid in the still. In addition, the large diameter of the internal tube of the column made it possible to carry out the rectification at a residual pressure of 0.5-1 mm (the pressure was measured with a McLeod gage).

For further work we used a fraction of constant boiling point and constant refractive index (Abbé refractometer), which consisted usually of not less than 80-90% of the charge. The subsequent purification of the hydrocarbons was carried out by adsorption on silica gel (ASK brand) from hexane solution. In the course of the desorption the desorbed solution was divided into 20-25 parts, for each of which, after removal of solvent by distillation, the refractive index was determined. For the final determination of various physicochemical constants of the hydrocarbons, fractions of identical refractive index were combined and they usually amounted to not less than 90% of the amount of hydrocarbon taken for adsorption.

By the combination of two methods of purification, i. e. a) fractional distillation with removal of impurities differing from the main product in molecular weight, and b) adsorption with removal of impurities differing in composition (mainly oxygen compounds), we succeeded in obtaining hydrocarbons of 98-99% purity. Purity was determined for the well-crystallizing 1,1-dicyclohexyldodecane on the basis of the crystallization curve and the determination of the cryoscopic constant. For the other, regrettably few, hydrocarbons capable

of being crystallized, the purity was estimated tentatively on the basis of the fusion curve, which was determined with the automatically recording Kurnakov photoregistering pyrometer [4]. By this method information was obtained at the same time on the melting (crystallization) points of the same hydrocarbons. It will be readily understood that for hydrocarbons that form glasses when cooled the purity can be estimated only tentatively, on the basis of the identity of the means of synthesis and purification of glass-forming and crystallizing hydrocarbons.

A detailed description of the conditions of synthesis will be given for the case of one hydrocarbon, 1,1-diphenyldodecane. This was prepared by the reaction of phenylmagnesium bromide with ethyl laurate. The reaction was carried out in a four-liter flask fitted with stirrer. A solution of 350 g (1.5 moles) of ethyl laurate in 200 ml of dry ether was added to a stirred solution of the organomagnesium compound obtained from 3.4 gram-atoms of magnesium and 535 g of bromobenzene in 850 ml of dry ether. The alkoxide was decomposed with water and 10% H_2SO_4 . The ether layer was washed with water and dried. Ether was distilled off, and the resulting 1,1-diphenyl-1-dodecanol was dehydrated in a vacuum (3-4 mm residual pressure) at 300°. We obtained 374 g (75% on the ethyl laurate) of 1,1-diphenyl-1-dodecene; b. p. 216-218° (7 mm); n_D^{20} 1.5420; d_4^{20} 0.9339; bromine value 49.7 (theoretical value 50.0). It should be particularly noted that the determination of bromine values by the Kaufmann method gives excellent results even for hydrocarbons of such high molecular weight and relatively complex structure as those prepared in the present investigation. In all cases the olefins synthesized had bromine values that were in excellent agreement with the theoretical values.

Part of the hydrocarbon was hydrogenated in hexane solution over Raney nickel at 70-80° and 150 atm in an autoclave.

The 1,1-diphenyldodecane obtained was fractionally distilled through a column and purified with the aid of silica gel. The other part of the 1,1-diphenyldodecene, also in hexane solution, was hydrogenated over Raney nickel at 150° and 150 atm in an autoclave. The 1,1-dicyclohexyldodecane was also fractionated and purified. For the other hydrocarbons we shall confine ourselves to references to the methods of synthesis and the amounts obtained: 1)* 7-Hexyloctadecane was prepared in an amount of 87 g by the reaction of hexylmagnesium bromide with ethyl laurate. 2) 7-Phenylloctadecane was prepared in an amount of 66 g by the reaction of hexylmagnesium bromide with dodecanophenone. The ketone was synthesized from phenylmagnesium bromide and laurionitrile. 3) 7-Cyclohexyloctadecane was prepared in an amount of 75 g by the hydrogenation of the preceding hydrocarbon. 4) 1,1-Diphenyldodecane. The synthesis of this is described above; it was obtained in an amount of 122 g. 5) 1,1-Dicyclohexyldodecane was prepared in an amount of 140 g by the hydrogenation of the preceding hydrocarbon. 6) 1-Cyclohexyl-1-phenyldodecane was prepared in an amount of 135 g by the action of cyclohexylmagnesium bromide on dodecanophenone. 7) 3-Heptyl-1,5-diphenylpentane was prepared in an amount of 165 g by the reaction of phenethylmagnesium bromide and ethyl hexanoate. 8) 1,5-Dicyclohexyl-3-heptylpentane was prepared in an amount of 132 g by the hydrogenation of the preceding hydrocarbon. 9) 1-Cyclohexyl-3-hexyl-6-phenylhexane was prepared in an amount of 89 g by the reaction of the organomagnesium compound formed from 3-cyclohexylpropyl bromide with 1-phenyl-3-nonanone. The ketone was prepared by oxidation of the alcohol synthesized from phenethylmagnesium bromide and heptanal. 10) 2,11-Diphenyldodecane was prepared in an amount of 56 g from methylmagnesium iodide and 1,10-diphenyl-1,10-decanedione. The diketone was synthesized from phenylmagnesium bromide and sebaconitrile. 11) 2,11-Dicyclohexyldodecane was prepared in an amount of 56 g by the hydrogenation of the preceding hydrocarbon. 12) 3-Benzyl-1,5-diphenylpentane was prepared in an amount of 35 g by the reaction of phenethylmagnesium bromide with ethyl phenylacetate. Found: C 91.76; 91.97; H 8.14; 8.05%. Calculated for $C_{24}H_{26}$: C 91.8; H 8.2%. 13) 1,5-dicyclohexyl-3-(cyclohexylmethyl)pentane was prepared in an amount of 70 g by the hydrogenation of the preceding hydrocarbon. 14) 3-(Cyclohexylmethyl)-1,5-diphenylpentane was prepared in an amount of 100 g by the reaction of phenethylmagnesium bromide and ethyl cyclohexylacetate. 15) 3-Benzyl-1,5-dicyclohexylpentane was prepared in an amount of 38 g by the reaction of 2-cyclohexylethylmagnesium bromide with ethyl phenylacetate. 16) 4-Cyclopentyl-1,7-diphenylheptane was prepared in an amount of 63 g by the reaction of 3-phenylpropylmagnesium bromide and ethyl cyclopentanecarboxylate. Cyclopentanecarboxylic acid was synthesized by the Grignard method from cyclopentylmagnesium bromide and carbon dioxide. 17) 1,7-Dicyclohexyl-4-cyclopentylheptane was prepared in an amount of 113 g by the hydrogenation of the preceding hydrocarbon. 18) 2-Heptyl-1,3-di-p-tolylpropane was synthesized in an amount of 38 g by the reaction of p-(bromomethyl)toluene

* The serial numbers of the hydrocarbons correspond to the serial numbers in Table 2.

TABLE 1

Formation of Diarylethanes and Relative Rates of Hydrolysis of Benzyl Chlorides and Benzyldiene Dichlorides

Halogen derivative	Yield of diarylethane %	Relative rate of hydrolysis of the benzyl chloride	Relative rate of hydrolysis of the corresponding benzyldiene dichloride
(Chloromethyl) benzene [Benzyl chloride]	5	1	1
o-(Bromomethyl) toluene	10	4,4	2,2
m-(Bromomethyl) toluene	—	1,2	6,7
p-(Bromomethyl) toluene	50	7,7	74
2-(Chloromethyl)-p-xylene	10	—	—
2-(Chloromethyl)mesitylene	95	—	800

[In this and similar cases it is to be presumed that the Grignard reagent derived from the halogen compound is to be understood, —Publisher] with ethyl octanoate. The bromo compound was prepared by the liquid-phase bromination of p-xylene at 130° with subsequent purification by means of rectification. 19) 2-Heptyl-1,3-bis-4-methylcyclohexylpropane was prepared in an amount of 17 g by the hydrogenation of the preceding hydrocarbon. 20) 2-Heptyl-1,3-di-o-tolylpropane was synthesized in an amount of 39 g from o-(bromomethyl)toluene and ethyl octanoate. The bromo compound was prepared from o-xylene. 21) 2-Heptyl-1,3-bis-2-methylcyclohexylpropane was prepared in an amount of 42 g by the hydrogenation of the preceding hydrocarbon. 2) 2-Pentyl-1,3-di-2,5-xylylpropane was synthesized in an amount of 70 g from 2-(chloromethyl)-p-xylene and ethyl octanoate. The chloro compound was prepared by the chloromethylation of p-xylene. 23) 1,3-Bis-2,5-dimethylcyclohexyl-2-pentylpropane was prepared in an amount of 56 g by the hydrogenation of the preceding hydrocarbon.

We must discuss also our attempt to synthesize 1,3-dimesityl-2-propylpropane. It was planned to carry out the synthesis of this hydrocarbon by the reaction of 2-(chloromethyl)mesitylene (prepared by the chloromethylation of mesitylene) with ethyl butyrate. However, by the action of magnesium on this chloro compound, instead of the expected organomagnesium compound, we obtained a 95% yield of the product of the condensation of two molecules of this chloro compound, 1,2-dimesitylethane, m. p. 118°. For this hydrocarbon the literature [5] gives m. p. 117–118°. Calculated for $C_{20}H_{26}$: C 90.20; H 9.80%. Found: C 89.94; H 9.90%. By the hydrogenation of this hydrocarbon we obtained the previously undescribed 1,2-bis-2,4,6-trimethylcyclohexylethane; b. p. 132° (0.5 mm); n_D^{20} 1.4790; d_4^{20} 0.8739. Here it was most interesting that from the hydrogenation products we succeeded in isolating (in 20% yield) an excellently crystallizing hydrocarbon, m. p. 118.5°. Calculated for $C_{20}H_{38}$: C 86.22; H 13.78%. Found: C 86.22; H 13.81%. We are at present continuing the investigation of this hydrocarbon; it appears to be one of the high-melting geometric isomers of 1,2-bis-2,4,6-trimethylcyclohexylethane. The liquid hydrogenation products (most probably a mixture of geometric isomers) freeze to a glass at about -40°.

In view of the unusual behavior of 2-(chloromethyl)mesitylene under the conditions for the preparation of the Grignard reagent, we must discuss the peculiar features found in the present work in the reaction of methylated benzyl halides with magnesium. It is known that multiple bonds in the β -position to halogen (e. g. in allyl halides) greatly increase the mobility of the halogen, which favors the coupling together of radicals in the process of the formation of the organomagnesium complex. An analogous, though considerably weaker, effect is possessed also by the aromatic nucleus, which results in a weakening of the carbon-halogen bond in (halomethyl)benzenes [5]. However, the reaction of benzyl chloride with magnesium proceeds quite satisfactorily with the formation of not more than 5–7% of bibenzyl. However, the introduction of methyl groups into the benzene nucleus, particularly in the p-position, greatly increases the mobility of the halogen, which immediately shows itself in an increased yield of the products of the side reaction, symmetrical diarylethanes [6]. Table 1 gives the amounts of diarylethanes obtained in the reaction of some substituted benzyl chlorides with magnesium. For comparison we give also values of the relative rates of hydrolysis in an aqueous-alcoholic medium of some methyl-substituted benzyl chlorides and benzyldiene dichlorides [7, 8].

As regards the other halogen compounds used in the present work, as would be expected their conversion into organomagnesium compounds and the further reactions of these with oxygen-containing reactants proceeded without appreciable complications. The hydrocarbons synthesized and their main properties are summarized in Table 2.

Of the various properties of the hydrocarbons given in Table 2, the most interesting are undoubtedly the viscosity-temperature characteristics. Though we cannot give a detailed discussion here of these data (the appropriate discussion is the subject of the paper [10]), we must draw attention to the considerably higher viscosities of aromatic hydrocarbons containing methyl groups in the nucleus than their monosubstituted isomers. This difference is so great that in some cases hydrogenation, i. e., conversion from an aromatic hydrocarbon into a cyclohexane, is accompanied by appreciable fall in viscosity, which is particularly marked at low temperature. On the other hand, according both to the data of the present work and to numerous data from investigations published previously [1], the hydrogenation of monosubstituted aromatic hydrocarbons is generally accompanied by a considerable rise in viscosity.

The determination of the ability of a given hydrocarbon to undergo crystallization is also of undoubted interest. It has been suggested previously [9] that for some organic compounds the main obstacle to crystallization is their high viscosity at low temperature. This property is manifested in a tendency for some hydrocarbons to undergo appreciable supercooling. This obstacle can be sometimes avoided by preparing crystals of the hydrocarbon beforehand by cooling it as a dilute solution in isopropyl alcohol. Seeding with these crystals brings about the rapid crystallization of the whole supercooled material. It is in this way that we prepared hydrocarbons No. 4 and 6 (Table 2) in a crystalline state. However, for most of the other noncrystallizing hydrocarbons this method was also unsuccessful since, when an alcoholic solution was cooled, the hydrocarbon came out as a liquid. It is still impossible to determine beforehand whether a given hydrocarbon is capable of being crystallized. This question is clearly associated closely with the difficult problem of the prior determination of the crystallization temperature of a hydrocarbon on the basis of its structure and molecular weight.

In this connection we must point out that even small changes in the structure of the hydrocarbon, which have scarcely any effect on the viscosity properties, may nevertheless affect the crystallization temperature very greatly. Thus, triphenylmethane $[\text{C}_6\text{H}_5-\text{C}]_3$ which was synthesized by Schiessler [2], turns into a glass at about -30° , whereas its closest homolog 3-benzyl-1,5-diphenylpentane $[\text{C}_6\text{H}_5-\text{C}-\text{C}]_2-\text{C}-\text{C}_6\text{H}_5$ which was prepared in the course of the present work, crystallizes excellently at $+54^\circ$.

Crystallization temperatures nevertheless show some regularities, particularly among hydrocarbons of a given homologous series. Thus, in particular the data on crystallization temperature obtained in the present work on 1,1-diphenyldodecane and 1,1-dicyclohexyldodecane agree well with the direct-proportionality relation between crystallization temperature and molecular weight characteristic for α, α -diphenylalkanes and α, α -dicyclohexylalkanes of composition $\text{C}_{20}-\text{C}_{30}$.

In conclusion we must mention that we have now completed the results of an investigation of various physicochemical properties of the above-described hydrocarbons and prepared them for the press. This investigation concerns mainly the spectral characteristics of the hydrocarbons in the infrared and ultraviolet regions and also the Raman spectra. We have made a detailed study also of the adsorption properties of the hydrocarbons and their mixtures under the conditions of chromatographic analysis.

SUMMARY

1. The syntheses and properties are described of twenty-three new C_{24} hydrocarbons of mixed structure.
2. Anomalies in the temperature-viscosity properties of polymethylbenzene derivatives were noted: it was found that aromatic hydrocarbons containing several methyl groups in the ring were considerably more viscous than their monosubstituted isomers.

TABLE 2
Properties of Hydrocarbons Synthesized

Number	Structural formula	Molecular B.p. (°C formula at 0.5mm)	n_D^{20}	d_4^{20}	Crystalliza- tion (glass) temp. (°C)	Viscosity (centipoises) at				
						150°	100°	50°	0°	-20°
1		$C_{14}H_{18}$	1,4481	0,7993	-0,3	0,92	1,87	5,2	29,0	—
2		$C_{14}H_{18}$	1,4800	0,8528	-5,4	1,14	2,1	6,5	38,3	—
3		$C_{14}H_{18}$	1,4634	0,8350	Below -60*	1,17	2,5	8,2	71,2	298
4		$C_{14}H_{18}$	1,5248	0,9244	+9,6	1,26	2,66	9,1	113**	653**
5		$C_{14}H_{18}$	1,4803	0,8758	+27,5	1,61	3,77	15,2	285**	—
6		$C_{14}H_{18}$	1,4990	0,8949	+3,3	1,56	3,34	13,8	251**	1860**
7		$C_{14}H_{18}$	1,5219	0,9246	Below -60*	1,20	2,32	7,1	65,3	361

TABLE 2 (Continued)

Number	Structural formula	Molecular formula	B.p. (°C) at 0.5mm	n_D^{20}	d_4^{20}	Crystallization (glass) temp. (°C)	Viscosity (centipoises) at			
							150°	100°	50°	0°
8		$C_{21}H_{24}$	170	1.4763	0.8664	Below -60*	1.58	3.6	15.2	239
9		$C_{21}H_{24}$	180	1.4971	0.8923	Below -60*	1.35	2.67	9.2	133
10		$C_{21}H_{24}$	181	1.5219	0.9237	-17.6	1.43	2.76	9.1	—
11		$C_{21}H_{24}$	173	1.4810	0.8757	Below -60*	1.88	4.09	15.3	215
12		$C_{21}H_{24}$	185	—	—	+54.5°	—	3.56	—	—
13		$C_{21}H_{24}$	179	1.4929	0.9042	-30*	2.48	7.35	61.7	9020
14		$C_{21}H_{24}$	186	1.5412	0.9666	-40*	1.66	3.57	15.4	315
15		$C_{21}H_{24}$	182	1.5158	0.9329	-40*	1.94	5.19	29.5	—

TABLE 2 (Continued)

Number	Structural formula	Molecular formula	B.p. (°C at 0.5 mm)	n_D^{20}	d_4^{20}	Crystallization (glass) temp. (°C)	Viscosity (centipoises) at			
							150°	100°	50°	0°
16		$C_{22}H_{22}$	186	1.5392	0.9663	Below -60*	1.56	3.23	12.4	165
17		$C_{22}H_{24}$	184	1.4911	0.9016	-50*	2.12	5.28	30.4	803
18		$C_{24}H_{26}$	184	1.5257	0.9223	-50	1.39	3.28	16.2	394
19		$C_{24}H_{28}$	166	1.4741	0.8647	-60*	—	3.64	17.7	—
20		$C_{26}H_{28}$	172	1.5300	0.9324	-40*	1.57	3.64	16.4	692
21		$C_{26}H_{30}$	166	1.4770	0.8706	-60*	1.46	3.43	15.9	501
22		$C_{26}H_{32}$	162	1.5347	0.9334	-25*	1.52	4.63	27.8	2660
23		$C_{26}H_{34}$	151	1.4746	0.8652	-60*	1.39	3.34	17.3	646

* Samples froze to a glass.

** In the supercooled state.

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CONDENSATION OF HEXACHLOROCYCLOPENTADIENE WITH UNSATURATED NITRO COMPOUNDS

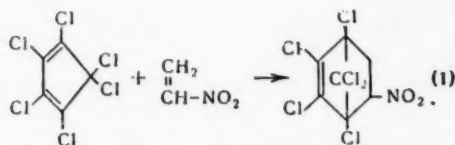
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 10, pp. 1858-1860, October, 1960
Original article submitted May 15, 1959

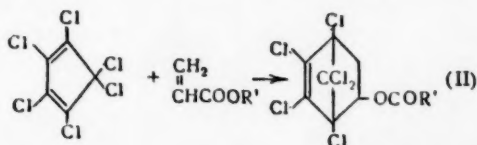
Only one compound has been reported which contains simultaneously chlorine atoms and a nitro group in its molecule and is obtained by the diene synthesis, namely the adduct formed by hexachloropentadiene with *m*-nitrostyrene [1]. Such compounds, however, may be of considerable interest from the point of view of physiological activity [2]. We considered it to be of interest to study the condensation of hexachlorocyclopentadiene with unsaturated nitro compounds. Of the latter, compounds of two types may be used: $\text{CH}_2 = \text{CHR}$ (in which $\text{R} = \text{e. g. NO}_2, \text{COOR}' - \text{NO}_2$) and $\text{NO}_2\text{CH} = \text{CHR}'$ (in which $\text{R}' = \text{e. g. H, alkyl, aryl, COOCH}_3, \text{CN}$). The presence of the sterically active voluminous chlorine atoms in hexachlorocyclopentadiene, particularly in the 5-position, renders its condensation with dienophiles difficult [3].

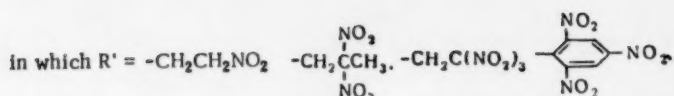
As Tamelen and Thiede showed [4], the nitro and methyl groups of 1-nitropropene are in the *trans* positions. This is clearly true also for other nitro dienophiles of the type $\text{NO}_2\text{CH} = \text{CHR}$. Diene condensation with such dienophiles will probably proceed with difficulty. On the basis of these facts it may be supposed that disubstituted nitro dienophiles of the type $\text{NO}_2\text{CH} = \text{CHR}$ would condense with hexachlorocyclopentadiene with very great difficulty. As regards monosubstituted nitro dienophiles it may be predicted that they will condense more readily with hexachlorocyclopentadiene than disubstituted nitro dienophiles, but the rate of such condensation will probably be low. The experimental results fully confirmed our suppositions.

When a solution of nitroethylene and hexachlorocyclopentadiene in chlorobenzene was heated at 100-102° for 14 hours, we obtained a good yield of 1,2,3,4,7,7-hexachloro-5-nitro-2-norbornene (I):



Good yields of the corresponding adducts were obtained also when hexachlorocyclopentadiene was heated for many (10-28) hours with 2-nitroethyl, 2,2-dinitropropyl, 2,2,2-trinitroethyl, and 2,4,6-trinitrophenyl acrylates:





On the other hand, all our attempts to cause hexachlorocyclopentadiene to react with 1-nitropropene, 2-nitropropene, β -nitrostyrene, methyl 3-nitroacrylate, and 3-nitroacrylonitrile were unsuccessful. When the components were heated together both in solvent (chlorobenzene, toluene, glacial acetic acid, propionitrile) and in absence of solvent, and also in presence of Cl_3CCOOH as catalyst, for as long as 20-30 hours, the diene was recovered unchanged quantitatively.

We decided to test our adducts, which contained chlorine atoms and nitro groups, for insecticidal activity, since it is known that many adducts synthesized from hexachlorocyclopentadiene and also various compounds containing both a chlorine atom and a nitro group in the molecule will function as insecticides. The tests* showed that all the adducts that we obtained show insecticidal activity.

EXPERIMENTAL

Condensation of Hexachlorocyclopentadiene with Nitroethylene. A solution of 7.3 g (0.1 mole) of nitroethylene, 9.03 g (0.033 mole) of hexachlorocyclopentadiene, and a little pyrogallol in 10 ml of chlorobenzene and 1 ml of glacial acetic acid was heated under reflux at 100-102° for 14 hours. When the reaction had ceased, solvent was vacuum-distilled off (12-15 mm) and unchanged hexachlorocyclopentadiene was steam-distilled off. When allowed to stand, the residue crystallized. Yield 8.4 g (73%). After being crystallized from aqueous methanol (one part of methanol to two parts of water) it had m. p. 160-161.5°. Found: C 24.94; 25.05; H 1.01; 1.27; N 4.21; 3.97; Cl 61.39; 61.14%. $C_7H_3NO_2Cl_6$. Calculated: C 24.27; H 0.867; N 4.04; Cl 61.56%.

Condensation of Hexachlorocyclopentadiene with 2-Nitroethyl Acrylate. A solution of 2.5 g (0.017 mole) of 2-nitroethyl acrylate, 4.7 g (0.017 mole) of hexachlorocyclopentadiene, and a little pyrogallol in 10 ml of chlorobenzene was boiled under reflux for 21 hours. When the reaction had ceased, low-boiling substances were vacuum-distilled off (12-15 mm). The residue crystallized when cool. The weight of adduct obtained was 6.4 g (89%). After being crystallized from aqueous alcohol (one part of water to two parts of alcohol) it had m. p. 93-94°. The condensation product (II) ($R' = CH_2CH_2NO_2$) is soluble in ether, alcohol, benzene, chloroform, and isopropyl alcohol; it is insoluble in water. Found: C 28.78; 28.78; H 1.81; 1.82; Cl 50.29; 50.29%. $C_{10}H_7NO_4Cl_6$. Calculated: C 28.70; H 1.67; Cl 50.88%.

Condensation of Hexachlorocyclopentadiene with 2,4,6-Trinitrophenyl Acrylate. A mixture of 12.55 g (0.046 mole) of hexachlorocyclopentadiene, 13.0 g (0.046 mole) of 2,4,6-trinitrophenyl acrylate, and a little pyrogallol was heated at 100-110° with stirring for 28 hours. When the reaction had ceased, unchanged diene (1.93 g) was steam-distilled off. The resinous residue was separated from water and dissolved in ether; the ethereal solution was dried with anhydrous sodium sulfate. Ether was distilled off under reduced pressure, and the residual oil crystallized. This gave 16.6 g (65%) of (II) ($R' = 2,4,6-(NO_2)_3C_6H_2$), m. p. 116.5-117.5° (from isopropyl alcohol). The adduct is soluble in alcohol, ether, benzene, and chloroform; it is insoluble in petroleum ether and water. Found: C 31.58; 31.32; H 1.25; 1.20; Cl 37.06; 36.86%. $C_{14}H_4O_8N_3Cl_6$. Calculated: C 32.19; H 0.89; Cl 38.30%.

Condensation of Hexachlorocyclopentadiene with 2,2-Dinitropropyl Acrylate. A mixture of 5.46 g (0.02 mole) of hexachlorocyclopentadiene, 4.08 g (0.02 mole) of 2,2-dinitropropyl acrylate, and a little pyrogallol was heated at 100-110° with stirring for ten hours. When cool, the reaction mixture crystallized. We obtained 9.5 g (about 100%) of (II) ($R' = CH_2C(NO_2)_2CH_3$). After being crystallized from alcohol it had m. p. 114-115°. The adduct is soluble in ether, benzene, and warm alcohol; it is insoluble in water. Found: C 27.97; 27.29; H 1.76; 1.80; Cl 44.60; 44.56%. $C_{11}H_8O_6N_2Cl_6$. Calculated: C 27.67; H 1.67; Cl 44.65%.

Condensation of Hexachlorocyclopentadiene with 2,2,2-Trinitroethyl Acrylate. A solution of 5.35 g (0.019 mole) of hexachlorocyclopentadiene, 4.6 g (0.019 mole) of 2,2,2-trinitroethyl acrylate, and a little pyrogallol in 15 ml of chlorobenzene was refluxed for 20 hours. When reaction ceased, solvent was vacuum-distilled off (12-15 mm) and unchanged diene was steam-distilled off. The resinous residue was separated from water, and dissolved in ether; the ethereal solution was dried with anhydrous sodium sulfate. Ether was distilled off, and

* Toxicological tests were carried out by N. M. Permyakova.

the residual oil crystallized after long standing. We obtained 7.2 g (72%) of (II) ($R' = \text{CH}_2\text{C}(\text{NO}_2)_3$). The condensation product is readily soluble in alcohol, ether, benzene, and isopropyl alcohol; it is insoluble in water. For purification the adduct was dissolved in boiling aqueous alcohol or hexane, from which it then separated as an oil, which crystallized on standing; m. p. 55-57°. Found: Cl 41.62; 41.31%. $\text{C}_{10}\text{H}_5\text{O}_8\text{N}_3\text{Cl}_6$. Calculated: Cl 41.92.

SUMMARY

1. Hexachlorocyclopentadiene was brought into reaction with unsaturated nitro compounds, and as a result some adducts were prepared for the first time.
2. It was suggested that steric hindrance exists in the diene condensation of hexachlorocyclopentadiene with unsaturated nitro compounds of the types $\text{RCH} = \text{CH}_2$ and $\text{NO}_2\text{CH} = \text{CHR}'$, and this hypothesis was confirmed.
3. The adducts synthesized possess insecticidal activity.

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KINETICS OF THE DEHYDRATION OF ALCOHOLS OVER
TRICALCIUM DIPHOSPHATE, AND THE DEACTIVATION
OF THE LATTER BY ORGANIC BASES

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 10, pp. 1861-1867, October, 1960

Original article submitted May 22, 1959

Readily available and cheap tricalcium diphosphate is receiving ever increasing recognition as an active, selective, stable, and readily regenerable catalyst for hydrolysis [1] and hydration [2] reactions. The dehydration of alcohols is also very rapid and selective over this catalyst [3].

In the present work we have made a fuller study of the effect of the position of the OH group in the alcohol molecule on the kinetics of the reaction. Over calcium phosphate, as over other catalysts, *t*-butyl alcohol is most readily dehydrated; then follow secondary alcohols, cyclohexanol and isopropyl alcohol; and the most difficult to dehydrate is ethanol. The olefins formed in presence of this catalyst are not isomerized or cracked. Thus, in the gaseous products of the dehydration of *t*-butyl alcohol the content of isobutene was found to be 98-99%. In the dehydration of cyclohexanol only cyclohexene was formed isomerization products (methylcyclopentenes) and irreversible-catalysis products (benzene, cyclohexane) were absent.

The activation energy for the dehydration of ethanol calculated from experimental data is greater than the activation energies for the dehydration of isopropyl and *t*-butyl alcohols. While the values of the activation energy E are equal for the dehydration of *t*-butyl alcohol and of isopropyl alcohol, the preexponential factor K_0 is greater in the first case. While the values of E are similar, K_0 for the dehydration of cyclohexanol is almost 100 times as high as for the dehydration of ethanol. Diisopropyl ether is less readily dehydrated than isopropyl alcohol, and K_0 for this reaction is about one-half as high, whereas the activation energies are close in value.

It was earlier supposed that the activity of a phosphate catalyst is due to its acidic nature [1]. In fact, in presence of bases (caustic alkali, triethylamine, pyridine) the activity of a phosphate catalyst in the hydrolysis of vinyl ethers is greatly reduced [4]; after treatment with potassium carbonate [3] or caustic alkali [5] it becomes inactive also for the dehydration of ethanol. In the present work we studied the effect of organic bases on the kinetics of the dehydration of alcohols in presence of a phosphate catalyst. As would be expected, when the catalyst is poisoned with nitrogenous bases the activation energy for the reaction, and therefore also the nature of the active surface of the catalyst, does not change. There is a reduction only in the value of K_0 , which characterizes the concentration of catalyst sites active in the reaction under investigation. The deactivating effect of triethylamine is considerably greater than that of the weaker base pyridine. The poisoning action of triethylamine and the reduction in K_0 indicates adsorptional displacement of alcohol by the base. These facts confirm the view of the acidic nature of a phosphate catalyst.

EXPERIMENTAL

The experiments were carried out under continuous-flow conditions. The alcohols were fed at constant rate into the reaction tube with the aid of an automatic doser [6]. The diameter of the tube was 18 mm, the

TABLE 1

Kinetics of the Dehydration of Ethyl, Isopropyl, and t-Butyl Alcohols

Alcohol being dehydrated, its constants	Rate of passage (ml/min)	Temp. (°C)	Rate of for- mation of olefins, m (ml/min)	Convers- ion of al- cohol into olefin (%)	Activation energy E (kcal/m)	Preexpo- nential factor K_0
95% ethanol d_4^{20} 0,8044	0,177	359	4,5	6,8	34,2	$3,4 \cdot 10^{12}$
	0,177	371	7,5	11,4		
	0,177	374	9,0	13,6		
	0,177	383	15,1	22,9		
	0,177	388	17,6	26,8		
	0,177	395	20,2	30,6		
	0,177	402	26,2	40,0		
	0,177	405	28,8	43,6		
	0,177	412	36,0	54,6		
Isopropyl alcohol b.p. 81,0—81,5° (750 mm) d_4^{20} 0,7877 n_D^{20} 1,3778	0,177	278	7,5	14,4	18,3	$1,3 \cdot 10^8$
	0,177	288	9,1	17,5		
	0,177	294	11,0	21,2		
	0,177	293	13,6	26,2		
	0,177	307	18,6	35,8		
	0,177	311	19,0	36,8		
	0,177	314	21,7	41,8		
	0,177	322	26,2	50,4		
	0,177	323	25,3	48,6		
	0,177	329	29,5	56,7		
	0,177	331	30,5	58,6		
	0,177	340	38,0	73,0		
t-Butyl alcohol b.p. 80—81,5° (745 mm) d_4^{20} 0,7872 n_D^{20} 1,3876	0,167	200	4,1	10,2	18,0	$7,8 \cdot 10^8$
	0,167	208	5,0	12,5		
	0,167	223	10,8	27,0		
	0,167	232	15,1	37,7		
	0,167	239	16,3	40,8		
	0,167	242	18,1	45,2		
	0,167	250	22,4	56,0		

volume of catalyst was 10 ml (5.9 g), and the grain dimensions were 2×1 mm. The catalyst was prepared from calcium chloride and diammonium phosphate; when the grain size of the catalyst was reduced its activity did not change. The temperature, which was maintained constant within $\pm 1^\circ$, was measured with a thermocouple, whose hot junction was placed in the catalyst layer. The constants of the alcohols used are given in Table 1. The liquid products of the dehydration of ethanol were collected in a trap cooled to -50° ; in experiments with other alcohols it was cooled with ice. The gaseous reaction products were collected in a gas buret over saturated sodium chloride solution; their composition was determined by gas chromatography on silica gel (gas carrier: carbon dioxide). In the experiments with isopropyl alcohol, diisopropyl ether, and t-butyl alcohol the amounts of olefins dissolved in the catalyzate were determined by the bromination method [7]. A particularly large amount of olefin was dissolved in the catalyzate at low conversions, because the solubility of an olefin depends greatly on the water content of the catalyzate. The catalyst was found to be highly stable, and the reproducibility of the experiments was good. After each series of experiments in presence of amines the catalyst was regenerated by treatment with air for two hours at 400° .

Kinetics of the Dehydration of Alcohols of Various Structures. The results of experiments on the dehydration of ethyl, isopropyl, and t-butyl alcohols, cyclohexanol, and diisopropyl ether are represented in Table 1

TABLE 2

Kinetics of the Dehydration of Diisopropyl Ether and Cyclohexanol

Compound being dehydrated, its contents	Rate of passage (ml/min)	Temp. (°C)	Rate of for- mation of olefins, m (ml/min)	Convers- ion into olefin (%)	Activation energy E (kcal/m)	Preexpo- nential factor K_0
Diisopropyl ether b.p. 68-68,5° (750 mm) d_4^{20} 0,7261 n_D^{20} 1,3687	0,326	260	7,4	7,0	15,8	$2,3 \cdot 10^7$
	0,326	264	8,7	8,2		
	0,326	268	9,4	8,9		
	0,326	286	16,7	15,8		
	0,326	307	25,0	23,6		
	0,326	307	24,6	23,2		
	0,326	319	35,0	33,0		
Cyclohexanol m.p. 22,5° n_D^{21} 1,4656	0,177	242	3,4*	8,2	32,0	$1,4 \cdot 10^{14}$
	0,177	252	6,0	15,8		
	0,177	262	10,2	28,4		
	0,177	271	17,5	46,5		
	0,177	284	34,6	91,0		

*Recalculated as gaseous form.

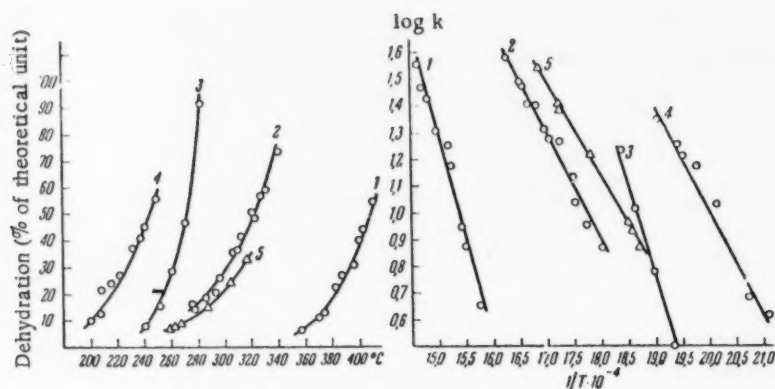


Fig. 1. Kinetics of the dehydration of alcohols and of diisopropyl ether over a phosphate catalyst: 1) ethanol; 2) isopropyl alcohol; 3) cyclohexanol; 4) t-butyl alcohol; 5) diisopropyl ether.

and 2 and in Fig. 1. In Fig. 1 the graphs on the left represent the temperature dependence of the conversion, and those on the right show the applicability of the Arrhenius equation to the kinetics of the reactions investigated. The temperature at which the dehydration of ethanol starts over this catalyst is about 100° above that for the dehydration of isopropyl alcohol and cyclohexanol and about 150° above the temperature of the decomposition of t-butyl alcohol. To characterize the readiness with which alcohols of different structures are dehydrated we may compare the temperatures at which 10% and 40% conversions are attained. For t-butyl alcohol these conversions are attained at 200° and 238°; for cyclohexanol at 244° and 270°; for isopropyl alcohol at 264° and 316°; and for ethanol at 368° and 402°. It will be seen from these data that t-butyl alcohol is dehydrated most readily, then follow the secondary alcohols, cyclohexanol and isopropyl alcohol. Water is least readily eliminated from the primary alcohol, ethanol.

TABLE 3

Kinetics of the Dehydration of Isopropyl Alcohol over a Catalyst Deactivated with Triethylamine (Rate of passage of alcohol-triethylamine mixture 0.177 ml/min)

Triethylamine content of alcohol		Temp. (°C)	Rate of formation of propene m (ml/min)	Conversion of alcohol into propene (%)	Activation energy E (kcal/mole)	Preexponential factor K_0
%	Molar ratio alcohol: amine					
1,28	130	284	6,7	13,0	18,0	$7,9 \cdot 10^7$
1,28	130	293	10,6	20,5		
1,28	130	318	17,3	33,2		
1,28	130	331	23,4	45,2		
1,28	130	342	28,2	54,2		
1,28	130	351	32,7	63,0		
6,4	26	288	6,6	13,5	17,0	$2,8 \cdot 10^7$
6,4	26	300	8,7	18,0		
6,4	26	317	13,4	27,4		
6,4	26	328	19,7	40,0		
6,4	26	349	28,0	57,0		

TABLE 4

Kinetics of the Dehydration of t-Butyl Alcohol over Catalysts Deactivated by Triethylamine and by Pyridine (Rate of passage of alcohol-amine mixture 0.167 ml/min)

Amine content of alcohol			Temp. (°C)	Rate of formation of isobutene (%)	Conversion of alcohol into isobutene (%)	Activation energy E (kcal/mole)	Preexponential factor K_0
Amine	%	Molar ratio alcohol: amine					
Triethylamine	1,29	105	211	4,0	10,0	17,2	$2,2 \cdot 10^8$
"	1,29	105	221	5,5	14,1		
"	1,29	105	233	8,2	20,5		
"	1,29	105	243	11,5	28,8		
"	1,29	105	249	13,6	34,0		
"	1,29	105	255	15,4	38,6		
Triethylamine	6,45	21,4	220	3,6	9,5	17,1	$1,2 \cdot 10^8$
"	6,45	21,4	234	5,3	14,0		
"	6,45	21,4	250	8,9	23,4		
"	6,45	21,4	263	14,1	37,2		
Pyridine	6,45	17,1	214	4,0	10,5	16,8	$1,3 \cdot 10^8$
"	6,45	17,1	230	6,5	17,0		
"	6,45	17,1	242	9,7	25,5		
"	6,45	17,1	248	12,7	33,4		
"	6,45	17,1	258	15,7	41,3		

Hence, the rates of dehydration of primary, secondary, and tertiary alcohols over calcium phosphate fall in the same order as for other catalysts for this reaction [8]. The investigation showed that the gaseous products of the dehydration of isopropyl and t-butyl alcohols contain 99% of propene and 98-99% of isobutene, respectively.

It is known that the preparation of cyclohexene by the dehydration of cyclohexanol over solid catalysts is often complicated by irreversible-catalysis reactions and the isomerization of cyclohexene into methylcyclo-

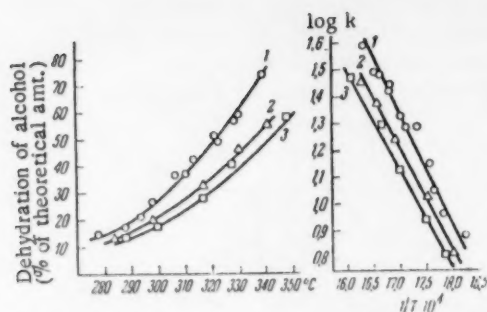


Fig. 2. Kinetics of the dehydration of isopropyl alcohol: 1) in absence of triethylamine; 2) in presence of 1.28% by weight of triethylamine; 3) in presence of 6.4% by weight of triethylamine.

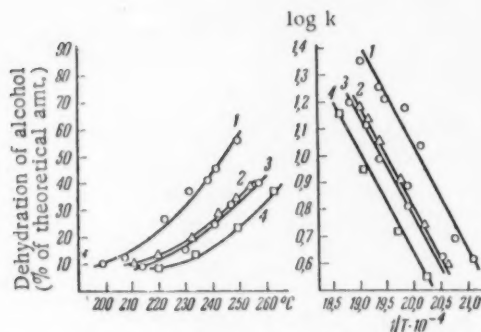


Fig. 3. Kinetics of the dehydration of t-butyl alcohol: 1) in absence of amines; 2) in presence of 1.29% by weight of triethylamine; 3) in presence of 6.45% by weight of triethylamine; 4) in presence of 6.45% of pyridine.

will be seen from Fig. 1, the dehydration of diisopropyl ether is slower than that of isopropyl alcohol. An analogous picture was observed in [3]: diethyl ether decomposes more slowly than ethanol.

Deactivation of the Catalyst by Organic Bases. Organic bases were added in definite amounts to the alcohols and passed with them over the catalyst. The amines used had the following constants: pyridine, b. p. 114-115° (752 mm), d_4^{20} 0.9775, and n_D^{20} 1.5088; triethylamine, b. p. 89-89.5° (752 mm), d_4^{20} 0.7260, and n_D^{20} 1.4005.

Data on the dehydration of isopropyl alcohol containing 1.28% and 6.4% of triethylamine are presented in Table 3 and Fig. 2. From Table 3 and Fig. 2 it follows that the presence of small amounts of triethylamine in the reaction zone results in a lowering of catalyst activity by 25-30%. However, a further fivefold increase in the triethylamine concentration has less effect on the reaction rate. The deactivating action of triethylamine is due to adsorptional displacement of alcohol by amine from the active catalyst surface. The deactivated catalyst rapidly regains its activity if pure isopropyl alcohol is passed over it under the conditions of reaction. This indicates the reversible character of the adsorption of triethylamine on the catalyst.

pentene [9]. Analysis of the catalyzates obtained in our experiments showed that the sole product of the reaction was cyclohexene (b. p. 82-83°; n_D^{20} 1.4448; d_4^{20} 0.8105), the yield of which already attained 91% at 284°. It will be seen that the phosphate catalyst shows high selectivity in the dehydration of alcohols.

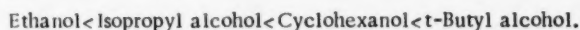
The reaction rate was measured as the rate of formation of olefins (\bar{m}). The activation energy E was calculated from the Arrhenius equation. It was shown by special experiments that in the range of space velocity of passage of alcohols of 9-12 ml/hr the rate of the formation of olefins remained constant. Hence, reaction rate does not depend on concentration of alcohol; the reaction is of zero order and the rate of formation of olefins can be regarded as the rate constant.

Fig. 1 shows that the Arrhenius equation is closely obeyed by all the reactions studied. The calculated activation energies are given in Table 1. The activation energy for the dehydration of isopropyl alcohol, i. e. when the hydrogen at the α -carbon is replaced by CH_3 , is greatly lowered (by 15.9 kcal/mole). However, the activation energy for the dehydration of a secondary alcohol of a different structure, cyclohexanol, is only 2.2 kcal/mole less than the activation energy for the decomposition of ethanol. The activation energy for the dehydration of t-butyl alcohol is similar to that for isopropyl alcohol. The values of the activation energy for the dehydration of ethanol obtained in the present work and in [2] are very close. As regards the values of the activations energies for the dehydration of isopropyl and t-butyl alcohols, they differ from those calculated in [3] because in this latter work no account was taken of the amounts of olefins dissolved in the catalyzate. The significance of these corrections will be seen from the fact that in our experiments, for example, at low conversions of t-butyl alcohol no isobutene separated, but was completely dissolved in the catalyzate. As

In Table 4 and Fig. 3 we give the results of experiments on the deactivation of the phosphate catalyst by triethylamine and by pyridine in the dehydration of t-butyl alcohol. In presence of 1.29% of triethylamine the extent of the dehydration of the alcohol at 240° was reduced by a factor of almost two, and in the experiment with 6.45% of triethylamine by a factor of 2.5-3. Hence, with the same concentration of triethylamine the rate of the dehydration of t-butyl alcohol is lowered to a considerably greater extent than the dehydration of isopropyl alcohol. This is probably to be explained on the view that a molecule of an alcohol containing a branched hydrocarbon group undergoes more powerful adsorptional displacement. Pyridine deactivates the catalyst to a considerably less extent: 6.45% of pyridine in the alcohol has about the same deactivating effect as 1.29% of triethylamine. The difference in the deactivating effects of pyridine and triethylamine is due to the fact that the latter is the stronger base and is more strongly adsorbed by the catalyst. It will be seen from Figures 2 and 3 that the Arrhenius equation is obeyed also in the dehydration of isopropyl and t-butyl alcohols in presence of catalyst poisons (amines). The closeness of values of activation energy for the reactions on the active and on the deactivated catalyst indicates the homogeneity of the active sites of the catalyst.

SUMMARY

1. The readiness with which alcohols are dehydrated over tricalcium diphosphate increases along the series:



2. The activation energies for dehydration were calculated, and they were found to have identical values for isopropyl and t-butyl alcohols (18 kcal/mole) and considerably higher values for ethanol and cyclohexanol (34 and 32 kcal/mole).

3. The dehydration of alcohols over a phosphate catalyst proceeds in an extremely selective fashion: the gaseous reaction products consist of olefins of high purity (98-99%). The cyclohexene formed by the dehydration of cyclohexanol does not contain products arising from isomerization or redistribution of hydrogen.

4. Addition of organic bases to the alcohol lowers the activity of the catalyst. Triethylamine has a considerably greater deactivating effect than pyridine. This confirms the hypothesis of the acidic nature of the activity of a phosphate catalyst.

5. The activation energy for the reaction over a catalyst poisoned with an organic base is the same as that over an active catalyst, which is an indication of the homogeneity of the active sites of the catalyst.

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BRIEF COMMUNICATIONS

LIMITATIONS IMPOSED BY CONDITIONS OF STABILITY ON THE DEPENDENCE OF ACTIVITY COEFFICIENTS ON COM- POSITION FOR BINARY SOLUTIONS OF NON-ELECTROLYTES

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 10, pp. 1868-1869, 1960

Original article submitted January 26, 1960

If a solution is in equilibrium at constant temperature and pressure then the condition for stability of equilibrium is given by the expression

$$\frac{\partial^2 Z}{\partial x_1^2} > 0; \quad \frac{\partial^2 Z}{\partial x_2^2} > 0. \quad (1)$$

Here Z is the isobaric-isothermal potential; x_1 and x_2 are the mole fractions of the first and second components in solution. Expression (1) imposes certain limitations on the dependence of the activity coefficients on composition of the solution. We have examined these limitations. On curves showing the dependence of activity coefficients on the composition of the solution, maxima and minima are sometimes found. This was first noted by Scatchard and Raymond for the chloroform-ethanol system [1] and was confirmed by Röck and Schröder [2]. However this is not the only system with extrema of the activity coefficients. Similar properties are also observed for other systems [3, 4].

First of all we will write expression (1) in an expanded form. The chemical potentials of the first and second components in a solution of nonelectrolytes will be:

$$\mu_1 = \mu_{10} + RT \ln \gamma_1 + RT \ln x_1, \quad (2)$$

$$\mu_2 = \mu_{20} + RT \ln \gamma_2 + RT \ln x_2, \quad (3)$$

where μ and γ are the chemical potential and activity coefficient respectively of a component. Since

$$\frac{\partial^2 Z}{\partial x_1^2} = \frac{\partial \mu_1}{\partial x_1} - \frac{\partial \mu_2}{\partial x_1}, \quad (4)$$

then, by calculation, after some rearrangement of (2) and (3) we find

$$\frac{\partial^2 Z}{\partial x_1^2} = \frac{\partial \ln \gamma_1}{\partial x_1} - \frac{\partial \ln \gamma_2}{\partial x_1} + \frac{1}{x_1 \cdot x_2}. \quad (5)$$

Expression (1) for the first component may be written as

$$\frac{\partial \ln \gamma_1}{\partial x_1} - \frac{\partial \ln \gamma_2}{\partial x_1} + \frac{1}{x_1 \cdot x_2} > 0. \quad (6)$$

Let the activity coefficient-composition curve have two extrema. From equation (6) it follows that on this curve there must be at least one point of inflection, i. e.

$$\frac{\partial^2 \ln \gamma_1}{\partial x_1^2} = 0 \quad (7)$$

If the extrema of the activity coefficient are located left and right of the abscissa $x_1 = x_2 = 0.5$, then the presence of a point of inflection can lead to a conflict with the original expression (1). The latter will always occur if the activity coefficients in dilute solution differ substantially from unity. Therefore the presence of two extrema of the activity coefficient indicates the imminence of separation of the solution into layers.

The conditions for stability also impose limitations on the limiting behavior of the activity coefficients. The Gibbs-Duheim equation for binary solutions can be written in the form

$$\frac{\partial \ln \gamma_1}{\partial x_2} = - \frac{x_2}{x_1} \frac{\partial \ln \gamma_2}{\partial x_2} \quad (8)$$

This equation permits six kinds of coefficients-composition dependence for limiting conditions which was shown generally for partial molar quantities by Krichevskii and Kazamovskii [5] and was considered for activity coefficients in [6, 7]. For the fifth and sixth types of limiting behavior of the activity coefficients according to Ebert and Kohler

$$\lim_{x_2 \rightarrow 0} \left| \frac{\partial \ln \gamma_1}{\partial x_2} \right| = + \text{const}, \quad (9)$$

$$\lim_{x_2 \rightarrow 0} \left| \frac{\partial \ln \gamma_1}{\partial x_2} \right| = + \infty. \quad (10)$$

If we write the condition for stability in the form of

$$\frac{\partial \mu_1}{\partial x_1} > 0, \quad (11)$$

then from (2) we obtain

$$-\frac{\partial \ln \gamma_1}{\partial x_2} + \frac{1}{x_1} > 0 \quad (12)$$

or

$$\lim_{x_2 \rightarrow 0} \left| \frac{\partial \ln \gamma_1}{\partial x_2} \right| + 1 > 0. \quad (13)$$

From eq. (13) we see that $\lim_{x_2 \rightarrow 0} \left| \frac{\partial \ln \gamma_1}{\partial x_2} \right|$ cannot have an infinitely large value (i. e. the sixth type cannot exist since it conflicts with the conditions of stability) and that it must be less than unity (i. e. limitations are imposed on the fifth type).

SUMMARY

1. Two extrema on activity coefficients-composition curves, occurring right and left of the abscissa $x_1 = x_2 = 0.5$, indicate the imminence of separation of the solution into layers.

2. The sixth type of limiting behavior of the activity coefficients conflicts with the conditions for stability, and limitations are imposed on the fifth type.

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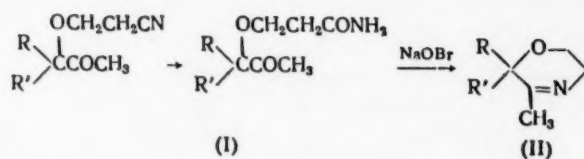
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PREPARATION OF DEHYDROMORPHOLINES FROM β -CYANOETHYL ETHERS OF ACETYLENIC ALCOHOLS

G. A. Shvekhgeimer

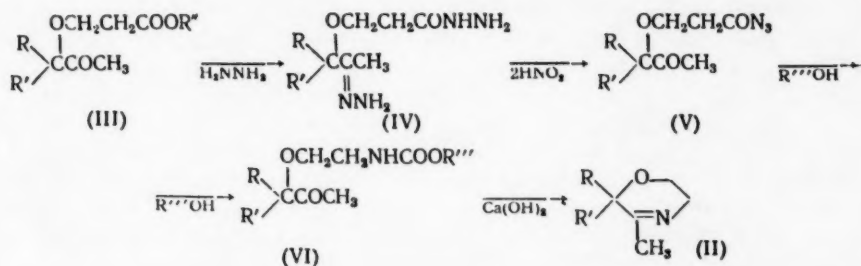
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 10, pp. 1870-1871, 1960
Original article submitted February 3, 1960

The route initially chosen for the preparation of dehydromorpholines may be represented by the following scheme:

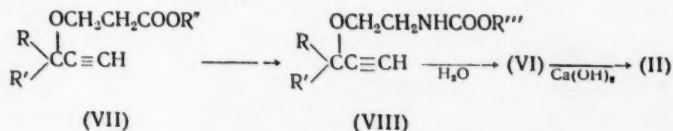


However, treatment of the derived keto-amide I ($\text{R} = \text{R}' = \text{CH}_3$) with sodium hypobromite yielded only bromoform. Consequently it was decided to study other routes for the preparation of dehydromorpholines.

Reaction of hydrazine hydrate with keto-esters (III) give hydrazonehydrazides (IV) which by reaction with nitrous acid are converted into ketoazides (V) [1], and the latter readily react with alcohols yielding ketourethanes (VI), hydrolysis of which with $\text{Ca}(\text{OH})_2$ affords the dehydromorpholines (II).



The possibility was also shown of preparing dehydromorpholines (II) by two other routes: 1) by treatment of the esters (VII) with hydroxylamine, $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ and $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$ [2], hydration to the urethanes (VIII), hydrolysis to the keto-urethanes (VI) and thence to (II); 2) by hydration of the urethanes (VIII) (prepared by another route [3]) to give (VI), with subsequent hydrolysis to (II).



EXPERIMENTAL

Preparation of the Keto-amide (I) ($R = R' = \text{CH}_3$). (a) The β -cyanoethyl ether of dimethylacetylcarbinol, 35 g, (b. p. 96-97° at 18 mm) [4] was added, with stirring, over 30 mins to a mixture of 400 ml of 40% H_2O_2 and 4 ml of 40% aqueous KOH solution. The temperature gradually rose to 50° and then began to drop. The reaction mixture was stirred one hour at 50°, cooled, saturated with potash, extracted with ethyl acetate and distilled. The Keto-amide (I), 30.2 g, b. p. 176-179° (6 mm) was obtained. Found: N 8.20; 8.23%, $\text{C}_8\text{H}_{15}\text{NO}_3$. Calculated: N 8.09%. (b) A mixture of 14.5 g of the amide of β -carboxyethyl ether of dimethylethynylcarbinol (m. p. 51-52°) [5], 25 ml of water and 1 g of mercury sulphate was stirred three hours at 90-95°, a further 1 g of mercury sulphate was added and the mixture stirred for two more hours at 95°. The reaction mass was saturated with potash and extracted with ethyl acetate. Keto-amide (I), 9.2 g, b. p. 178-182° (8 mm) was obtained.

Preparation of 2,2,3-Trimethyl-3,4-Dehydromorpholine (II) ($R = R' = \text{CH}_3$). (a) To a solution of 57 g of the ether (III) ($R = R' = R'' = \text{CH}_3$) [6] in 120 ml of absolute alcohol was added 35 g of hydrazine hydrate, during which the mixture became warm. The mixture was boiled for 10 hours and low-boiling substances were distilled off under vacuum. The hydrazone-hydrazide (IV), 61 g, ($R = R' = \text{CH}_3$) was obtained. To a solution of 61 g ($R = R' = \text{CH}_3$) in 110 ml of water at 10-15° was added a solution of 51 ml of concentrated sulfuric acid in 225 ml of water and then 200 ml of ether. To the mixture at 8-10° a solution of 42 g of sodium nitrite in 120 ml of water was added with energetic stirring. The ethereal layer was separated, the aqueous layer extracted three times with ether and the bulked ethereal solutions dried with magnesium sulfate. The dried ethereal solution of keto-azide (V) ($R = R' = \text{CH}_3$) was added to 225 ml of absolute alcohol, the ether distilled off, and the alcoholic solution boiled for eight hours. The alcohol was distilled off, to yield 22 g of the keto-urethane (VI) ($R = R' = \text{CH}_3$, $R'' = \text{C}_2\text{H}_5$).

A mixture of 22 g of (VI), 70 g of calcium oxide and 30 ml of water was heated in a Wurtz flask fitted with a Babo funnel until distillation of water ceased. To the cooled flask was added 35 ml of water and the mixture was again heated until distillation ceased. The distillates were bulked, saturated with potash, carefully extracted with ether, dried and distilled. There was obtained 6.2 g of 2,2,3-trimethyl-3,4-dehydromorpholine (II) ($R = R' = \text{CH}_3$) b. p. 143-147°; 62-66° (32 mm); n_D^{20} 1.4408; d_4^{20} 0.9350. Found: C 66.31; 66.38; H 10.11; 10.27; N 10.61; 10.73%. $\text{C}_7\text{H}_{13}\text{NO}$. Calculated: C 66.14; H 10.23; N 11.02%. The picrate had m. p. 178-181° (from alcohol). Found: N 15.96; 15.81%, $\text{C}_{13}\text{H}_{16}\text{N}_4\text{O}_8$. Calculated: N 15.73%. (b) A mixture of 29 g of the urethane (VIII) ($R = R' = \text{CH}_3$, $R'' = \text{C}_2\text{H}_5$) [3], 25 ml of water, 100 ml of dioxan, 5 ml of concentrated sulfuric acid and 2 g of mercury sulfate was refluxed for three hours, 2 g of mercury sulfate was added, and reflux continued for three more hours; after cooling 26 g of 40% aqueous NaOH and 300 ml of ether were added. The keto-urethane, 22.5 g (VI) ($R = R' = \text{CH}_3$, $R'' = \text{C}_2\text{H}_5$) was obtained from the ethereal extract. Hydrolysis of the keto-urethane was carried out as described above (70 g of calcium oxide and two 50 ml portions of water were used). The dehydromorpholine, 5.8 g, (II) ($R = R' = \text{CH}_3$), b. p. 63-67° (32 mm) was obtained. (c) To a mixture of 21 g of $\text{HCl} \cdot \text{H}_2\text{NOH}$, 34 g of the ether (VII) ($R = R' = R'' = \text{CH}_3$) [7] and 150 ml methanol at 18-20°, a solution of 14 g of sodium in 180 ml of methanol was added, and the whole stirred 12 hours at 20° and 18 hours at 50-55°. On cooling, 10 g $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ and 48 g $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$ were added, and the mixture stirred eight hours at 20°. The methanol was distilled off in vacuum, 200 ml of water was added to the residue, the solution saturated with potash and extracted successively with ether, benzene and ethyl acetate. The extracts were bulked, and the low boiling compounds distilled off, during which 6.5 g of the original ether (VII) distilled over. The urethane, 25 g, (VIII) ($R = R' = R'' = \text{CH}_3$) was obtained, which by hydration and subsequent hydrolysis over CaO was converted into the dehydromorpholine (VI) ($R = R' = \text{CH}_3$).

Preparation of 2,3-Dimethyl-2-Ethyl-3,4-Dehydromorpholine (II) ($R = \text{CH}_3$, $R' = \text{C}_2\text{H}_5$). A mixture of 30 g of the keto-ether (III) ($R = \text{CH}_3$, $R' = \text{C}_2\text{H}_5$), 20 g hydrazine hydrate and 130 ml of absolute alcohol refluxed for 15 hours, yielded 32.6 g of the hydrazide-hydrazone (IV) ($R = \text{CH}_3$, $R' = \text{C}_2\text{H}_5$). From a mixture of 32.2 g of (IV), 300 ml of water, 30 ml of concentrated sulfuric acid and 150 ml of ether, and a solution of 22 g sodium nitrite in 50 ml of water at 0-5°, an ethereal solution of the keto-azide (V) ($R = \text{CH}_3$, $R' = \text{C}_2\text{H}_5$) was obtained, which after addition of 150 ml of absolute alcohol and distilling off the ether, was refluxed two hours; the alcohol was then distilled off, to yield 29 g of the keto-urethane (VI) ($R = \text{CH}_3$, $R' = R'' = \text{C}_2\text{H}_5$). Hydrolysis of 19 g of the keto-urethane (70 g of CaO and two 35 ml portions of water were used) yielded 6 g 2,3-dimethyl-2-ethyl-3,4-dehydromorpholine (II) ($R = \text{CH}_3$, $R' = \text{C}_2\text{H}_5$), b. p. 167-170°, 74-78° (26 mm); n_D^{20} 1.4517; d_4^{20} 0.9478. Found:

C 68.32; 68.41; H 10.52; 10.73; N 9.51; 9.68%. $C_8H_{15}NO$. Calculated: C 68.08; H 10.64; N 9.93%. Picrate m. p. 198-200° (from alcohol). Found: N 15.37; 15.30%. $C_{14}H_{18}N_4O_8$. Calculated: N 15.14%.

SUMMARY

A method has been developed for the synthesis of dehydromorpholines from β -cyanoethyl ethers of acetylenic alcohols.

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THE CATALYTIC EFFECT OF MERCAPTANS ON THE CONVERSION OF BORONTRIALKYL BY MEANS OF AMMONIA, AMINES AND ALCOHOLS

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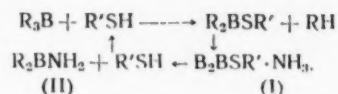
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1872-1873, 1960

Original article submitted March 1, 1960

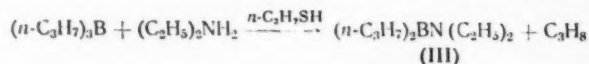
By passing ammonia into the *n*-butyl ester of di-*n*-butylthioborinic acid at 150°, we obtained di-*n*-butylboramine [1]. During a further study of this reaction we have found that the esters of dialkylthioborinic acids react with ammonia with vigorous evolution of heat at room temperature and even when cooled. At first a white crystalline complex $R_2BSR \cdot NH_3$ (I) was formed, which readily decomposed at a temperature of ~20° with liberation of the mercaptan and formation of the dialkyl (amino) boron II.

The facile reaction of the thioesters R_2BSR' with ammonia permitted the synthesis of any dialkyl (amino) boron R_2BNH_2 from the boron trialkyl, using a catalytic amount of mercaptan. Thus, by passing ammonia into tri-*n*-butyl boron or tri-iso-amylboron, containing ~1/25 equivalent of *n*-butyl-mercaptan, di-*n*-butyl (amino) boron and di-iso-amyl (amino) boron were obtained in 70-75% yield.



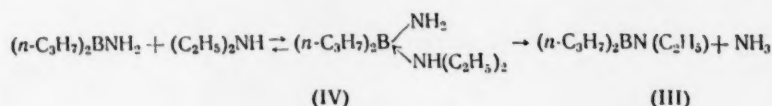
where $R = n-C_4H_9$, $i-C_5H_{11}$; $R' = n-C_4H_9$.

The thioester, which was formed as a result of the first reaction, on interaction with ammonia regenerated the mercaptan which entered into further reaction with the boron trialkyl and the process repeated until the trialkyl boron was completely converted. By this method it was possible to synthesize also *N*-substituted dialkyl (amino) borons. Thus by addition of diethylamine to tri-*n*-propyl boron, containing *n*-propylmercaptan, di-*n*-propyl (diethylamino) boron (III) was obtained in 92% yield.

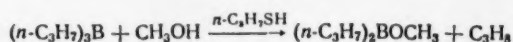


The reaction was accompanied by a vigorous spontaneous evolution of heat (85-90°) which was adequate for its completion. It may be noted that by addition of the mercaptan to a (1 : 1) mixture of boron trialkyl and amine under these conditions the amine (III) was not formed, since the complex $R_3B \leftarrow NHR_2$ was obtained the decomposition of which was brought about at 170-200° [2]. The first member of the series of dialkyl (amino) borons, dimethyl (amino) boron, which exists as a dimer, m. p. 9°, was first prepared by Wiberg and coworkers [3]. Booth and Kraus [4] and also Evers and coauthors [5] reported the preparation of di-*n*-butyl (amino) boron. Comparison of the properties of the compounds obtained by them with the properties of the di-*n*-butyl (amino)

boron synthesized by us makes it evident that the authors mentioned were not handling this compound. The dialkyl (amino) borons are liquids which catch fire in air. Determination of the molecular weight cryoscopically in benzene showed that they are monomers. The dialkyl (amino) borons react with alcohols to form crystalline ammoniate esters of dialkylborinic acid, which in vacuum are converted into the esters of dialkylborinic acid. With substituted amines they undergo a transamination reaction, which takes place through intermediate formation of the complex compound (IV). Thus by heating a mixture of di-n-propyl (amino) boron with diethylamine, di-n-propyl (diethylamino) boron was synthesized.



By employing the catalytic property of mercaptans in the reaction of boron trialkyls with alcohols, it was possible to prepare, under mild conditions, esters of dialkylborinic acids, including a number of methyl esters R_2BOCH_3 not readily available.



EXPERIMENTAL

All operations were carried out under nitrogen.

Di-n-butyl (amino) boron. Tri-n-butylboron, 56.4 g (0.31 M) and 2 ml of n-butyl-mercaptan were placed in a two-necked flask fitted with a reflux condenser and dry ammonia passed into the reaction mass for 1.5 hours. During this time the mixture became hot (70°) and spontaneously maintained this temperature for ~ 15 min. Towards completion of the passage of ammonia the contents of the flask were heated at 110-135°. After double fractionation of the liquid reaction products, 30.2 g (69.2%) of di-n-butyl (amino) boron, b. p. 63-65° (15 mm); n_D^{20} 1.4277 was obtained. Earlier this compound had been obtained by us from the butyl ester of di-n-butyl-thioboric acid and ammonia, and had b. p. 55-55.6° (11 mm) n_D^{20} 1.4278 (I).

Di-iso-amyl (amino) boron. In a way analogous to that described above, 12.6 g (0.057 M) of tri-iso-amyl boron, containing 1 ml n-butylmercaptan (duration of experiment 25 min) yielded 7.1 g (74.7%) of di-iso-amyl (amino) boron, b. p. 70-73° (8mm). After redistillation, the compound had 74-75° (10mm); n_D^{20} 1.4298; d_4^{20} 0.7701; Found: C 70.87; 70.79; H 14.17; 14.15; B 6.54; 6.64%. M 168.5; 169.3. $C_{10}H_{24}BN$. Calculated: C 71.01; H 14.30; B 6.40%; M 169.2.

Di-n-propyl (diethylamino) boron. Reaction of Diethylamine with Di-n-propyl (amino) boron. A mixture of 6.83 g (0.06 M) of di-n-propyl (amino) boron and 7.2 ml (0.07 M) of diethylamine was heated to boiling in a flask fitted with a reflux condenser for 2.5 hours. The ammonia, 0.88 g (97.8%), was condensed in a trap, cooled with a mixture of dry ice and acetone. The reaction mixture was fractionated in vacuum giving 9.1 g (89.2%) of di-n-propyl (diethylamino) boron, b. p. 119-122° (96 mm). After redistillation the compound had b. p. 92-93° (34 mm); n_D^{20} 1.4323; d_4^{20} 0.7702. Found: C 71.08; 71.02; H 14.32; 14.17; B 6.67%. $C_{10}H_{24}BN$. Calculated: C 71.01; H 14.30; B 6.40%.

Reaction of Tri-n-propylboron with Diethylamine in the Presence of n-Propylmercaptan. To a mixture of 15.7 g (0.112 M) of tri-n-propylboron and 2 ml n-propyl-mercaptan there was added in the course of 20 minutes, 12 ml (0.117 M) of diethyl amine at such a rate that the temperature of the reaction mass was spontaneously maintained at ~ 85-90°. The mixture was then heated 10 min at the same temperature, 2500 ml of gas, containing 0.095 M of propane was liberated. After fractionation of the liquid reaction products 17.3 g (91.9%) of di-n-propyl (diethylamino) boron, b. p. 77-79° (16 mm) was obtained.

All the prepared dialkyl (amino) borons were mobile, colorless liquids, soluble in organic solvents. They were inflammable in air and were hydrolyzed.

Methyl Ester of Di-n-Propylborinic Acid. To a solution of 13.4 g (0.096 M) of tri-n-propyl boron in 4.5 ml (0.11 M) of methyl alcohol was added 1 ml n-butyl-mercaptan. The mixture became hot (40°). The reaction mass was heated for six hours at 65-70°. 1880 ml of gas containing 0.07 M propane was liberated. After frac-

tionation, 9.45 g (77.5%) of the methyl ester of di-n-propylborinic acid, b. p. 54-56° (44 mm); n_D^{20} 1.4028 was obtained. Earlier this compound was obtained by us from the n-propyl ester of di-n-propylthioborinic acid and had b. p. 55.5-56° (44 mm); n_D^{20} 1.4027 [1, 6].

SUMMARY

1. In the presence of catalytic amounts of mercaptans borontrialkyls react with ammonia, amines and alcohols at 20-100° with formation of the dialkyl (amino) borons, the N-substituted compounds or the ester dialkyl borinic acids respectively.

2. With substituted amines dialkyl (amino) borons undergo a transamination reaction.

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EFFECT OF TEMPERATURE ON THE REACTION OF ALKENES
WITH DIAZOACETIC ESTER IN THE PRESENCE OF COPPER
SULFATE

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 10, pp. 1874-1876, October, 1960
Original article submitted March 2, 1960

Continuing the study of the reaction of diazoacetic ester with ethylene derivatives, in the present work we examined the effect of temperature on the formation of ethyl alkylcyclopropanecarboxylates, which we have already reported [1]. This problem has now acquired particular importance as syntheses with diazoacetic ester lead to cyclopropane derivatives, which are attracting increasing attention from investigators because they have been studied little and have unusual properties, conferred on them by the three-membered carbon ring. This reaction was carried out previously with very diverse ethylene derivatives: esters of unsaturated acids [2-4], vinyl ethers [5], cyclic hydrocarbons containing a double bond in the ring [6-7] or in a side chain [8], dienes [9], etc. Such a wide range of compounds with very diverse chemical and physical properties makes it impossible to observe the effect of temperature on the course of the reaction reasonably accurately. For this reason, we used normal α -alkenes of various molecular weights. This made it possible to study the effect of the reaction temperature on the yield of ethyl 2-alkylcyclopropanecarboxylates.

On examining the results obtained in combination with the results of the reaction of 1-hexene with diazoacetic ester, which was studied previously [1], we came to the conclusion that 90-110° is the optimal temperature for the reaction of diazoacetic ester with alkenes. At 60-65°, considerable amounts of products are formed from condensation of only the biradicals $>\text{CHCOOC}_2\text{H}_5$ themselves. At a temperature above 110°, there is an increase in tar formation by the reaction products. It should be noted that the effect of temperature on the reaction was found to be more determinative than the effect of an increase in the molecular weight of the starting alkenes. Thus, ethyl 2-octylcyclopropanecarboxylate was formed in a higher yield at 100-110° than ethyl 2-butylcyclopropanecarboxylate at 60-65°, though in general, the reactivity is known to fall with an increase in molecular weight. A comparison of the physical properties of the compounds obtained shows that an increase in the size of the alkyl chain leads to a decrease in density and an increase in molecular refraction. Hydrolysis of the ethyl esters synthesized with an alcohol solution of alkali yielded the corresponding 2-alkylcyclopropanecarboxylic acids. The Raman spectra of all the ethyl 2-alkylcyclopropanecarboxylates were taken by our co-workers of the optical group of the G. K. Gaivoronskaya Laboratory of Hydrocarbon Chemistry.

An examination of the spectra shows that the compounds obtained were pure and did not contain isomerization products, i. e., esters of α,β -unsaturated acids (characteristic frequencies of 1640-1675 cm^{-1} were absent). The Raman spectra were as follows with $\Delta\nu$ in cm^{-1} .

1. Ethyl 2-amylycyclopropanecarboxylate. 145 (2); 175 (1); 227 (1 b); 665 (0); 735 (2 b); 790 (1 b); 810 (1); 832 (3 b); 860 (4 b); 880 (0 b); 890 (1 b); 923 (2 b); 967 (0); 985 (1 b) 1027 (1 b); 1043 (3 b); 1073 (0); 1123 (3); 1172 (1); 1210 (4 b); 1268 (1); 1304 (1); 1332 (2 b); 1406 (1 b); 1445 (8 b); 1462 (10 b); 1724 (4); 2850 (5); 2870 (3 b); 2897 (6); 2930 (6); 2955 (2); 2974 (2); 3000 (6); 3081 (3).

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2. Ethyl 2-hexylcyclopropanecarboxylate. 735 (0); 796 (1); 812 (1); 835 (2); 860 (2); 878 (0 b); 890 (1); 925 (0 b); 930 (1 b); 980 (0); 1022 (1 b); 1043 (1 b); 1074 (1 b); 1107 (1 b); 1133 (2 b); 1174 (1 b); 1212 (3 b); 1270 (1); 1305 (1 b); 1410 (1 b); 1446 (5 b); 1460 (5 b); 1724 (3 b); 2874 (2 b); 2900 (2 b); 2935 (3); 2975 (4 b); 3008 (4); 3083 (2).

3. Ethyl 2-octylcyclopropanecarboxylate. 677 (0); 725 (1 b); 833 (3); 860 (3); 880 (1); 977 (0 b); 1030 (1); 1041 (3); 1076 (1); 1115 (2 b); 1125 (3 b); 1175 (0); 1212 (3 b); 1248 (1 b); 1270 (1 b); 1302 (4); 1412 (1); 1440 (8 b); 1455 (8 b); 1725 (4); 2850 (6); 1895 (5 b); 2932 (6); 2968 (2); 3007 (2); 3082 (2).

EXPERIMENTAL

Starting compounds. 1-Heptene, 1-octene, and 1-decene were obtained by pyrolysis of the acetates of the corresponding primary alcohols at 490-520°. 1-Heptene: b. p. 93°; d_4^{20} 0.6958; n_D^{20} 1.4003; literature data [10]: b. p. 93.6°; d_4^{20} 0.6970; n_D^{20} 1.3998. 1-Octene: b. p. 120°; d_4^{20} 0.7172; n_D^{20} 1.4095; literature data [10]: b. p. 121.2°; d_4^{20} 0.7185; n_D^{20} 1.4087. 1-Decene: b. p. 170°; d_4^{20} 0.7438; n_D^{20} 1.4240; literature data [10]: b. p. 170.3°; d_4^{20} 0.7408; n_D^{20} 1.4215.

Ethyl 2-amylycyclopropanecarboxylate. Into a flask fitted with a stirrer, dropping funnel, and reflux condenser were placed 400 g (~4 mole) of 1-heptene and 4 g of CuSO_4 . A solution of 57 g (0.5 mole) of diazoacetic ester in an equal volume of 1-heptene was added dropwise to the boiling alkene (93°). After the addition, the mixture was cooled and filtered to remove the CuSO_4 . The excess alkene was removed in vacuum. The residue was distilled. We obtained 50 g of ethyl 2-amylycyclopropanecarboxylate. The yield was 54.3% of theoretical on the diazoacetic ester taken. Ethyl 2-hexyl- and 2-octylcyclopropanecarboxylates were obtained analogously (see table).

2-Amylycyclopropanecarboxylic acid. A 4-g sample of KOH was dissolved in 40 ml of hot $\text{C}_2\text{H}_5\text{OH}$. Then 10 g of the corresponding ethyl ester was added. The mixture was boiled with stirring for 25-30 hr and then evaporated. The salt was treated with 5% sulfuric acid. The organic acid was extracted with diethyl ether, dried with Na_2SO_4 , and distilled. We obtained 7 g of the acid. The ethyl esters of 2-hexyl- and 2-octylcyclopropanecarboxylic acids were hydrolyzed similarly (see table).

SUMMARY

1. Ethyl 2-amyly-, 2-hexyl-, and 2-octylcyclopropanecarboxylates and the corresponding acids were prepared for the first time.
2. The reaction of diazoacetic ester with normal α -alkenes gives the best yields at 90-110°.

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CONDENSATION OF NITROALKANES WITH 2,2-DIMETHYL- β -HYDROXYPROPIONALDEHYDE AND 2,2-DIMETHYL- β -HYDROXYBUTYRALDEHYDE

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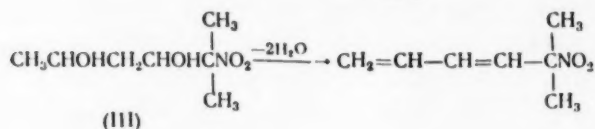
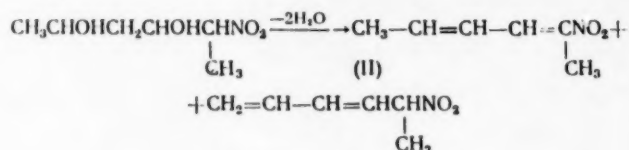
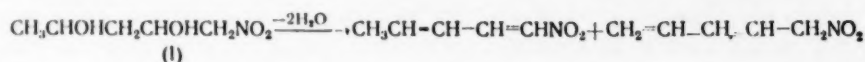
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*.

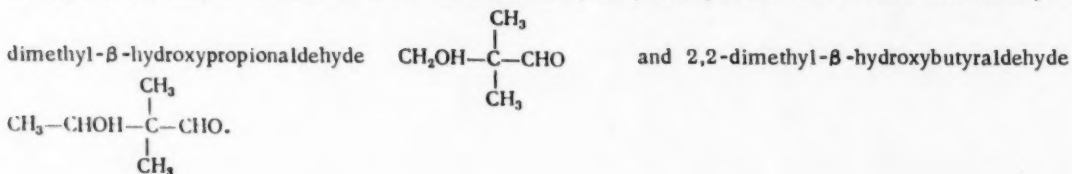
No. 10, pp. 1876-1878, October, 1960

Original article submitted March 3, 1960

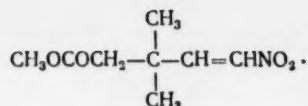
In a previous communication [1] we showed that CH_3NO_2 , $\text{C}_2\text{H}_5\text{NO}_2$, and $(\text{CH}_3)_2\text{CHNO}_2$ condense with acetaldoI in the presence of $\text{Ba}(\text{OH})_2$ to form the corresponding mononitrodiols (I, II, and III). Dehydration of these nitrodiols yielded the corresponding nitrodienes.



It seemed interesting to condense these nitroalkanes with hydroxy aldehydes of different structure, namely, 2,2-

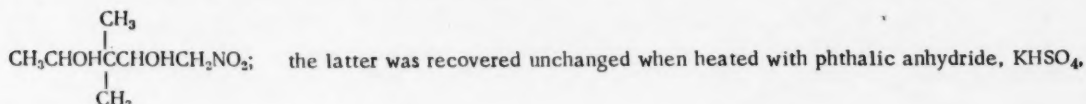


The reaction of 2,2-dimethyl-8-hydroxypropionaldehyde with CH_3NO_2 formed 1-nitro-3,3-dimethylbutane-2,4-diol $\text{CH}_2\text{OH}-\text{C}(\text{CH}_3)_2\text{CHOHCH}_2\text{NO}_2$, which was isolated in the form of colorless crystals. Treatment of 1-nitro-3,3-dimethylbutane-2,4-diol with ketene in ether and vacuum distillation of the acetylation product yielded 1-nitro-3,3-dimethyl-4-acetoxy-1-butene:



The condensation product of 2,2-dimethyl- β -hydroxypropionaldehyde and 1,1-dinitroethane was obtained as a viscous oil, which could not be distilled or isolated in a pure form. Treatment of this diol with acetic anhydride in the presence of H_2SO_4 formed a complex mixture of substances.

Attempts to condense 2,2-dimethyl- β -hydroxypropionaldehyde with $\text{CH}_3(\text{NO}_2)_2$ led to unstable compounds, which could not be distilled or purified by other methods. The condensation of 2,2-dimethyl- β -hydroxybutyraldehyde with CH_3NO_2 in methanol in the presence of $\text{Ba}(\text{OH})_2$ formed 1-nitro-3,3-dimethylpentane-2,4-diol



and $p\text{-C}_7\text{H}_7\text{SO}_3\text{H}$; the bulk of the product was converted to tar. Treatment of 1-nitro-3,3-dimethylpentane-2,4-diol with ketene yielded 1-nitro-3,3-dimethyl-4-acetoxy-1-pentene and 1-nitro-3,3-dimethyl-2,4-di-acetoxypentane, which could not be converted to 1-nitro-3,3-dimethyl-1,4-pentadiene by distillation with CH_3COONa .

EXPERIMENTAL

Condensation of 2,2-dimethyl- β -hydroxypropionaldehyde with nitromethane. A solution of 12 g of 2,2-dimethylhydroxypropionaldehyde (m. p. 88-89°) in 45 ml of CH_3OH was added from a dropping funnel to a stirred mixture of 8.5 g of CH_3NO_2 and 1 g of $\text{Ba}(\text{OH})_2$. The reaction mixture was kept at $\sim 20^\circ$ for two days and then diluted with water, neutralized with H_2SO_4 , filtered free from BaSO_4 , and extracted with ether. The ether solution was dried with Na_2SO_4 and the ether removed in vacuum to yield 1-nitro-3,3-dimethylbutane-2,4-diol as a viscous oil; the yield was 18 g; n_D^{20} 1.4770; treatment with dry ether and ligroin yielded crystals with m. p. 57-57.5°. Found: C 43.91; 43.83; H 7.79; 7.75; N 8.99; 9.07%. $\text{C}_6\text{H}_{14}\text{O}_4\text{N}$. Calculated: C 44.17; H 8.0; N 8.6%.

Acetylation of 1-nitro-3,3-dimethylbutane-2,4-diol. Into a solution of 1-nitro-3,3-dimethylbutane-2,4-diol (m. p. 57-57.5°) in 25 ml of ether was passed ketene (10-15% excess). Afterwards the ether solution was dried with Na_2SO_4 , the ether removed in vacuum, and the residual oil distilled to yield 1.8 g of 1-nitro-3,3-dimethyl-4-acetoxy-1-butene with b. p. 135° (2 mm) and n_D^{20} 1.4730; molecular weight found 182.7; calculated 187; Found: N 7.04; 7.25%. $\text{C}_{10}\text{H}_{18}\text{O}_6\text{N}$. Calculated: N 7.49%.

Condensation of 2,2-dimethyl- β -hydroxypropionaldehyde with 1,1-dinitroethane. To a mixture of 12 g of 1,1-dinitroethane, 60 ml of CH_3OH , and 1 g of $\text{Ba}(\text{OH})_2$ was added 10.5 g of 2,2-dimethyl- β -hydroxypropionaldehyde in small portions and the mixture stirred at $\sim 20^\circ$ for a day. The precipitate was removed by filtration and the filtrate diluted with 25 ml of water, acidified with dilute H_2SO_4 , and extracted with ether. Removal of the ether from the ether solution in vacuum and distillation of the low-boiling fractions yielded an oil, which could not be distilled or crystallized; the yield was 16 g; n_D^{20} 1.4470.

The oil obtained (16 g) was dissolved in 50 ml of $(\text{CH}_3\text{CO})_2\text{O}$, 2 drops of conc. H_2SO_4 added, and the mixture cooled and left at 20° . After 24 hr. the mixture was extracted with ether and the ether solution washed with NaHCO_3 solution, dried with Na_2SO_4 , and distilled. Removal of the low-boiling fractions yielded 2.2 g of a substance with b. p. 67.5° (0.02 mm), n_D^{20} 1.4310; d_4^{20} 1.0789; molecular weight found 164. This substance could not be identified.

Condensation of 2,2-dimethyl- β -hydroxybutyraldehyde with nitromethane. To a mixture of 10 g of CH_3NO_2 , 30 ml of CH_3OH , and 1 g of $\text{Ba}(\text{OH})_2$ was added 15 g of 2,2-dimethyl- β -hydroxybutyraldehyde (b. p. 80-90° (28 mm); n_D^{20} 1.4510] from a dropping funnel and the mixture stirred at 20° for 28 hr. The mixture was diluted with 25 ml of water, made weakly acid to litmus with H_2SO_4 , filtered free from BaSO_4 , and extracted with ether. The ether solution was dried with Na_2SO_4 and vacuum distilled. We obtained 4 g of 1-nitro-3,3-dimethylpentane-2,4-diol with b. p. 83-85° (2 mm); n_D^{20} 1.4526; d_4^{20} 1.099; Found:MR 43.50; Calculated:MR 43.20. Found: N 8.73; 8.73%. $\text{C}_7\text{H}_{15}\text{O}_4\text{N}$. Calculated: N 7.9%.

Acetylation of 1-nitro-3,3-dimethylpentane-2,4-diol. A solution of 10.5 g of unpurified 1-nitro-3,3-dimethylpentane-2,4-diol in 50 ml of ether was saturated with ketene with cooling in iced water. The ether was then removed in vacuum and the residue vacuum distilled to yield 4.5 g of 1-nitro-3,3-dimethyl-4-acetoxy-1-pentene with b. p. 85.5° (1.5 mm), n_D^{20} 1.4730. Found: C 53.04; 53.27; H 7.90; 7.79; N 7.13; 7.96%. $C_9H_{15}O_4N$. Calculated: C 53.04; H 7.90; N 7.00%.

In addition to 1-nitro-3,3-dimethyl-4-acetoxy-1-pentene, we isolated 1.5 g of 1-nitro-3,3-dimethyl-2,4-diacetoxypentane with b. p. 134-135° (1.5 mm); n_D^{20} 1.4690. Found: C 50.74; 50.53; H 8.01; 8.02; N 6.15; 6.29%. $C_{11}H_{19}O_6N$. Calculated: C 50.57; H 7.28; N 5.36%.

SUMMARY

1. 2,2-Dimethyl- β -hydroxypropionaldehyde and 2,2-dimethyl- β -hydroxybutyraldehyde react with CH_3NO_2 to form the corresponding condensation products 1-nitro-3,3-dimethylbutane-2,4-diol and 1-nitro-3,3-dimethylpentane-2,4-diol.

2. Acetylation of these diols with ketene gave 1-nitro-3,3-dimethyl-4-acetoxy-1-butene from 1-nitro-3,3-dimethylbutane-2,4-diol and 1-nitro-3,3-dimethyl-4-acetoxy-1-pentene and 1-nitro-3,3-dimethyl-2,4-diacetoxypentane from 1-nitro-3,3-dimethylpentane-2,4-diol.

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CATALYTIC HYDROGENATION OF SILICON-CONTAINING

β - AND γ -NITRILES

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 10, pp. 1878-1881, October, 1960
Original article submitted March 9, 1960

γ -Aminopropylsilanes containing hydrolyzable groups at the silicon atom are valuable intermediates [1]. The preparation of γ -aminopropylsilanes by catalytic hydrogenation of the corresponding β -cyanoethylsilanes has not been described in the literature. The results we obtained in previous work on the catalytic hydrogenation of silicon-containing γ -dinitriles to the corresponding silicon-containing δ -diamines over a skeletal nickel catalyst [2] gave grounds for hoping that an analogous method might be used for preparing monoaminoalkylsilanes and, in particular, representatives of the most interesting class of aminoalkylsilanes with alkoxy groups at the silicon atom from the corresponding cyanoalkylsilane compounds. It should be noted that β -cyanoethyltrialkoxysilanes are readily obtained from accessible β -cyanoethyltrichlorosilane [3] by treatment of the latter with alcohols [4].

The starting cyanosilanes, β -cyanoethyltrimethylsilane $(\text{CH}_3)_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{CN}$, γ -cyanopropyl-methyldimethoxysilane $\text{CH}_3-\text{Si}(\text{CH}_3\text{O})_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CN}$, and β -cyanoethyltriethoxysilane $(\text{C}_2\text{H}_5\text{O})_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{CN}$ were obtained by methods described previously [5,2,4]; their constants corresponded to literature data. β -Cyanoethyltrimethoxysilane $(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{CN}$ was obtained in 75-85% yield from $\text{Cl}_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{CN}$ by the action of absolute methanol in the presence of pyridine; it had b. p. 103-105° (10 mm); n_D^{20} 1.4130; d_4^{20} 1.0573. for $\text{C}_6\text{H}_{13}\text{O}_3\text{NSi}$. Found: Si 15.7; C 41.5; H 7.7%. Calculated Si 16.0; C 41.1; H 7.5%. This compound has not been described in the literature.

The nitriles were hydrogenated in a 0.175-liter rotating steel autoclave by the method we described previously [2]. The reaction products were separated from the catalyst by decantation and fractionated in vacuum after removal of the solvent. The amine content of separate fractions, determined by titration of samples of them in 50% alcohol with 0.1 N HCl solution, was 92-100° (Table 1). In experiments with solvent (CH_3OH or $\text{C}_2\text{H}_5\text{OH}$), the volume ratio of solvent to nitrile was 1 : 1. The nitriles containing alkoxy groups at the silicon atom were hydrogenated in absolute alcohol to prevent hydrolysis of the alkoxy groups.

We investigated the effect of catalyst composition, reaction conditions, and structure of the cyanoalkylsilane molecule on the amine yield. We first studied the hydrogenation of cyanoalkylsilanes without alkoxy groups and then that of cyanoalkylsilanes with two and three alkoxy groups at the silicon atom. The experimental conditions and results are given in Table 1. The amine yield given was calculated on the nitrile taken for the reaction and the remainder consisted of a high-boiling, viscous residue. The constants of the amines obtained are given in Table 2. As Table 1 shows, the course of the reaction and the yield of amines obtained depended to a considerable extent on the composition of the catalyst used. A comparison of the hydrogenation results obtained in experiments 1 and 2, 4 and 6, 13, 14, and 15, which were carried out on skeletal cobalt and nickel and Pt/C, shows that skeletal cobalt catalyst has a higher selectivity [6] than skeletal nickel both in the reduction of silicon-containing nitriles to primary amines and in the hydrogenation of silicon-free aliphatic nitriles, while the platinum catalyst directs the reaction predominantly toward the formation of secondary amines [7].

TABLE 1

Conditions of Hydrogenation of Silicon-Containing Nitriles

Exp. no.	Nitrile formula	A-mount of nitrile, g	Catalyst	Amount of catalyst, g	Nitrile: ammonia moles	Solvent	Temp, °C	Initial hydrogen pressure, atm.	Primary amine		Secondary amine	
									yield, wt. %	content in fraction, %	yield, wt. %	content in fraction, %
1	(CH ₃) ₂ Si-CH ₂ -CH ₂ -CN	11,5	Skeletal Ni	3	1:4	CH ₃ OH	80	75	57	100	0	—
2	The same	5	Skeletal Co	3	1:4	CH ₃ OH	75	75	87	98,2	0	—
3	"	6	Skeletal Co	3	**	CH ₃ OH	75	75	80	99,1	0	—
4	CH ₃ -Si(OCH ₃) ₂ -CH ₂ -(CH ₂) ₂ CN	7,5	Skeletal Ni	3	1:4	CH ₃ OH	75	115	56	99,3	0	—
5	The same	8,5	Skeletal Co	3	**	CH ₃ OH	75	115	41	98,5	36	99
6	"	20,5	Skeletal Co	6	1:3	CH ₃ OH	75	120	85	98,3	0	—
7	(OCH ₃) ₂ Si-CH ₂ -CH ₂ -CN	14	Skeletal Co	3	1:1,4	CH ₃ OH	80	100	***	—	—	—
8	The same	6,5	Pt/C	0,2	1:2	CH ₃ OH	120	140	31	92,2	0	—
9	"	13	Skeletal Ni	3	**	CH ₃ OH	80	140	***	—	—	—
10	(OC ₂ H ₅) ₂ Si-CH ₂ -CH ₂ -CN	23,5	Skeletal Ni	10	1:1,6	CH ₃ OH	75	90	—	—	—	—
11	The same	11	Skeletal Co	5	1:3	CH ₃ OH	80	115	***	—	—	—
12	"	19	Pt/C	0,2	1:5	CH ₃ OH	80	145	***	—	—	—
13	"	13,5	Pt/C	0,2	**	CH ₃ OH	150	145	12	96,4	33	104
14	"	10	Skeletal Ni	5	**	CH ₃ OH	80	100	49	96,3	37	105
15	"	9,5	Skeletal Co	5	**	CH ₃ OH	80	100	68	97,0	0	—
16	(OC ₂ H ₅) ₂ Si-CH ₂ -CH ₂ -CN	24	Skeletal Co	6	**	Without solvent	80	100	40	97,1	25	106

* Determined acidometrically.

** Reaction in the absence of ammonia.

*** Reaction mixture polymerized.

TABLE 2

Properties of Silicon-Containing Primary Amines Obtained

Formula	Constants of primary amines			MR _D	
	b.p., °C (mm Hg)	n_D^{20}	d_4^{20}	Found	Calculated
(CH ₃) ₃ Si-CH ₂ -CH ₂ -CH ₂ -NH ₂	55(27)	1,4300	0,7915	42,94	43,01
CH ₃ -Si(OCH ₃) ₂ -CH ₂ -CH ₂ -CH ₂ -NH ₂	58-60(4) 74(6,5)	1,4330	0,9430	49,1	48,8
(CH ₃ O) ₂ Si-CH ₂ -CH ₂ -CH ₂ -NH ₂	67(5) 91-92(15,5)	1,4235	1,0265	44,79	45,29
(C ₂ H ₅ O) ₂ Si-CH ₂ -CH ₂ -CH ₂ -NH ₂	68(3) 92(9)	1,4225	0,9506	59,20	59,18

The effect of ammonia on the direction of the reaction and the product yield depends on the nature of the catalyst and the number of alkoxy groups at the silicon atom in the molecule of the nitrile hydrogenated.

In the hydrogenation of β - and γ -cyanoalkylsilanes without alkoxy groups (experiments 2 and 3) or with two alkoxy groups at the silicon atom (experiments 5 and 6) and also in the hydrogenation of silicon-free nitriles, ammonia suppresses the formation of secondary amines [8].

However, in the hydrogenation of β -cyanoethylalkoxysilanes with three alkoxy groups at the silicon atom in the presence of ammonia, the expected amine could not be isolated; the reaction mixture polymerized (experiments 7, 8, and 10-12), probably due to ammonolysis of the silicon-alkoxy bond. β -Cyanoethyltrialkoxysilanes were therefore hydrogenated in absolute alcohol in the absence of ammonia (experiments 9 and 13-16).

Table 1 also shows that in the hydrogenation of β -cyanoethyltrialkoxysilane in the presence of solvent (ethanol) we obtained 68% of the primary amine and no secondary amine was isolated (experiment 15), while in the absence of solvent under the same conditions, we obtained 40% of the primary amine and 25% of the secondary amine. The solvent apparently acted as a diluent, which decreased the probability of interaction of the intermediate hydrogenation product (imino compound) with the amine formed.

SUMMARY

1. β -Cyanoethyl- and γ -cyanopropylsilanes were hydrogenated to the corresponding primary amines over metal catalysts.
2. As in the hydrogenation of silicon-free aliphatic nitriles, the hydrogenation was most selective over a skeletal cobalt catalyst.
3. The presence of ammonia and solvent promoted the formation of primary amines. β -Cyanoethyltrialkoxysilanes could be hydrogenated only in the absence of ammonia.

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SYNTHESIS OF SOME MIXED ESTERS OF THIOPHOSPHORIC ACID

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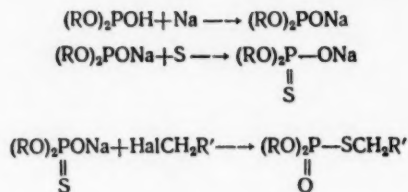
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1881-1883, October, 1960

Original article submitted March 11, 1960

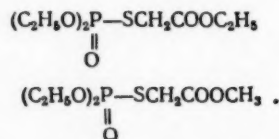
An important position among the great number of organophosphorus insecticides is occupied by various sulfur-containing esters of phosphorus acids and, in particular, mixed esters of thiophosphoric acid. Some representatives of O,O-dialkyl S-1,2-dicarbalkoxyethyl thiophosphates have been described in the literature as extremely effective acaricides and insecticides [1]. To study the insecticide properties and physiological activity we synthesized some O,O-dialkyl S-carbalkoxymethylthiophosphates. A study of the insecticide properties of the esters we obtained showed that some of them have a high insecticidal activity (table). We have not yet studied the acaricide properties. The esters we obtained were also studied as antiglaucoma agents.

We prepared the esters of O,O-dialkyl S-carbalkoxymethylphosphinic acids according to the following scheme:



where R = C₂H₅, i-C₃H₇, n-C₄H₉ and R' = COOC₂H₅, COOCH₃, CN.

To determine the structures of the compounds obtained more accurately, we plotted the Raman and infrared absorption spectra of the two following compounds:



In both cases there was an intense infrared absorption band of a P-O bond with a maximum at 1260 - 1266 cm⁻¹. At the same time, the Raman spectra showed no lines of appreciable intensity at 600 cm⁻¹, which would have been expected for a P=S bond. The triol structure demonstrated for the compounds obtained agrees with the conclusions of Kabachnik et al. [2] on esters of alkylthiophosphinic acids.

Formula	b.p., °C (P, mm Hg)	n_D^{20}	d_4^{20}	MR		P analysis		Yield %	Toxicity (granary weevil) solution conc., %	mortality after 7 days, %
				Calcu- lated	Found	Calcu- lated	Found			
$(C_4H_9O)_2P(=O)SCH_2COOCH_3$	129 (3)	1,4645	1,2192	55,10	54,85	12,81	12,92 12,93	26,0	0,05 0,1	100 100
$(C_4H_9O)_2P(=O)SCH_2COOC_2H_5$	138 (3)	1,4622	1,1826	59,71	59,57	12,11	12,12 12,26	71,7	0,05 0,1	95 100
$(C_4H_9O)_2P(=O)SCH_2CH_2COOCH_3$	137 (3)	1,4640	1,1867	59,73	59,55	12,11	12,30 12,24	30,5	0,05 0,1	0 0
$(i-C_4H_9O)_2P(=O)SCH_2COOCH_3$	134 (3)	1,4568	1,1203	68,95	69,05	10,92	11,03 10,93	66,0	0,05 0,1	0 0
$(C_4H_9O)_2P(=O)SCH_2COOC_2H_5$	150, (2,5)	1,4642	1,0984	78,19	78,43	9,94	9,83 9,85	40,0	0,05 0,1	2 12
$(C_4H_9O)_2P(=O)SCH_2CN$	132-135 (3)	1,4700	1,1970	49,16	48,71	14,83	15,10 15,09	24,0	0,01 0,05 0,1	$\frac{32}{100}$ 100 100/18hr

EXPERIMENTAL

Synthesis of diethyl carbethoxymethyl thiophosphate. To the sodium diethyl phosphite obtained from 8.5 g of sodium and 50 g of diethyl phosphite in 250 ml of ligroin was added 11.6 g of sulfur. After the mixture had been heated for an hour, 60.5 g of bromoacetic ester was added dropwise to the precipitated salt. The reaction mixture was then heated for 2 hr, the precipitate removed by filtration, the ligroin evaporated, and the residue vacuum distilled. We obtained 60.7 g of diethyl carbethoxymethyl thiophosphate with the constants given in the table. By analogous syntheses we also prepared diethyl carbomethoxymethyl thiophosphate, diethyl β -carbomethoxyethyl thiophosphate, diisopropyl carbethoxymethyl thiophosphate, dibutyl carbethoxymethyl thiophosphate, and diethyl cyanomethyl thiophosphate, whose constants are given in the table.

SUMMARY

Six esters of O,O-dialkyl S-carbalkoxymethylphosphinic acids that have not been described in the literature were prepared and their structures demonstrated.

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INTERNAL COMPLEX ACETYLACETONATES OF DIALKYLBORIC ACIDS

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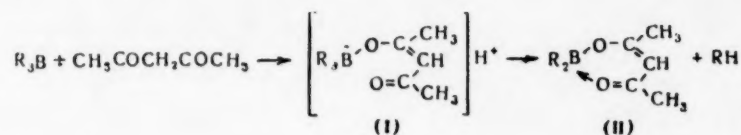
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 10, pp. 1883-1885, October, 1960

Original article submitted March 11, 1960

We showed that esters of dialkylboric acids are readily formed by the action of alcohols on trialkylborons [1, 2] or esters of dialkylthioboric acids [3, 4]. In the present communication we describe conversions of tri-*n*-propyl- and tri-*n*-butylborons, the *n*-butyl ester of di-*n*-butylthioboric acid, and the methyl ester of di-*n*-propylboric acid under the action of acetylacetone.

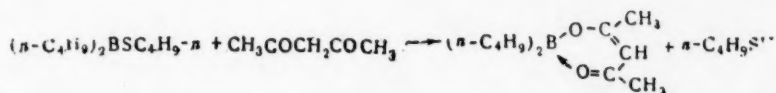
The reaction of tri-*n*-propylboron or tri-*n*-butylboron with acetyl-acetone yielded the acetylacetonates of the corresponding dialkylboric acids (II).



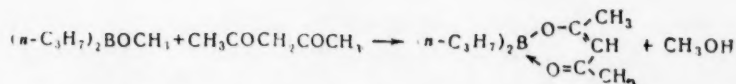
where $R = n\text{-C}_3\text{H}_7$ or $n\text{-C}_4\text{H}_9$.

The process occurred in the following way. After a brief induction period, which was apparently necessary for enolization of the acetylacetone and the formation of the boric acid (I), a vigorous reaction began and was accompanied by strong heat evolution. The anion of the boric acid (I) formed in the first stage of the reaction lost the radical R^\cdot in the form of an anion, which combined with a proton to give a saturated hydrocarbon, and was converted to compound (II).

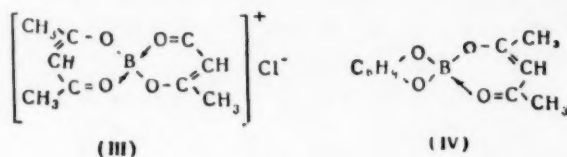
The acetylacetonate of di-*n*-butylboric acid was also synthesized by heating the *n*-butyl ester of di-*n*-butylthioboric acid and acetylacetone.



A third convenient method of synthesizing compounds of type (II) was transesterification. Thus, heating a mixture of the methyl ester of di-*n*-propylboric acid and acetylacetone yielded the acetylacetonate of di-*n*-propylboric acid.



Acetylacetonates of organoboron compounds have been unknown up to now. However, even in 1905, Dilthey obtained a heteropolar compound containing a monovalent boronium complex (III) by the action of acetylacetonate on BCl_3 [9]. This and other analogous derivatives of boron were investigated later by Bellamy et al. [10]. Schäfer and Braun [11] synthesized the orthoborate derivative (IV).



All operations were carried out in a nitrogen atmosphere.

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112.5-113.5° (14 mm); n_D^{20} 1.4660; d_4^{20} 0.8938. Found: C 67.40; 67.37; H 10.71; 10.54; B 5.60%. $C_{11}H_{21}BO_2$. Calculated: C 67.37; H 10.79; B 5.52%.

The acetylacetonate of di-n-propylboric acid was a yellow-green liquid, which was soluble in organic solvents. It was hydrolyzed in air but not oxidized. The refractive index hardly changed when the substance was stored for a month in a flask with a calcium chloride tube.

From the methyl ester of di-n-propylboric acid. Into a Favorskii flask were placed 4.63 g (0.035 mole) of the methyl ester of di-n-propylboric acid and 4 ml (0.039 mole) of acetylacetonone. Spontaneous heat evolution was observed. The solution was light green. The reaction mixture was heated at 110-120° (bath temperature) for 15 min. About 1 ml of methanol distilled. Fractionation in vacuum yielded 6.48 g (91.3%) of the acetylacetonate of di-n-propylboric acid with b. p. 103-105° (8 mm); n_D^{20} 1.4653.

Acetylacetonate of di-n-butylboric acid. From the n-butyl ester of di-n-butylthioboric acid. Into a flask with a distillation condenser was placed 8.46 g (0.04 mole) of the n-butyl ester of di-n-butylboric acid and 6 ml (0.058 mole) of acetylacetonone added. The mixture spontaneously evolved heat very strongly. The reaction mixture was heated at 150-190° for half an hour. n-Butyl mercaptan (3.46 g, 97%) was liberated. The residue was fractionated in vacuum. We obtained 7.8 g (88.5%) of the acetylacetonate of di-n-butylboric acid with b. p. 134-135° (13 mm); n_D^{20} 1.4667; d_4^{20} 0.888. Found: C 68.95; 69.10; H 11.09; 11.15; B 5.04; 4.99%. $C_{13}H_{25}BO_2$. Calculated: C 69.65; H 11.24; B 4.85%.

The acetylacetonate of di-n-butylboric acid was a mobile yellow liquid, which had a weak odor of acetylacetonone, was soluble in organic solvents, and was hydrolyzed in air.

From tri-n-butylboron. To 6.46 g (0.035 mole) of tri-n-butylboron in a flask with a reflux condenser was gradually added 4 ml (0.039 mole) of acetylacetonone and the mixture heated at 170-175° (bath temperature) for 30 min. Fractional distillation yielded 6.61 g (83.1%) of the acetylacetonate of di-n-butylboric acid with b. p. 123-125° (8 mm).

The infrared spectra were plotted on an IKS-14 spectrophotometer with a layer thickness of 0.1 mm and a CCl_4 solution concentration of ~5%.

The authors would like to thank B. V. Lopatin for plotting the spectra.

SUMMARY

Internal complex acetylacetonates of dialkylboric acids are readily obtained by the action of acetylacetonone on trialkylborons and esters of dialkylthioboric and dialkylboric acids.

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SYNTHESIS OF MERCAPTALS

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 10, pp. 1886-1887, October, 1960

Original article submitted March 21, 1960

In recent years an extensive study has begun of the reactions of aldehyde acetals and vinyl ethers and their use for the preparation of various polyene compounds [1-3]. In particular, in the work of Mikhailov, Ter-Sarkisyan, and Povarov it was shown that the condensation of acetals of aromatic aldehydes and ketones with unsaturated ethers readily yields aliphatic-aromatic ether acetals, unsaturated aldehydes, and aryl derivatives of polyene hydrocarbons [4-6].

However, in some cases, especially with unsaturated aldehydes, the preparative use of acetals is hampered by the difficulty of obtaining them. Meanwhile, the sulfur analogs of acetals, mercaptals, are readily obtained by the action of mercaptans on aldehydes and ketones in the presence of acid catalysts. In this connection, we synthesized mercaptals, mainly of unsaturated aldehydes, for studying the condensations of these compounds with α, β -unsaturated ethers, which have not been studied up to now. There are only a few reports in the literature on the synthesis of mercaptals of unsaturated aldehydes [7, 8]. It is interesting to note that according to literature data [8], crotonaldehyde adds a mercaptan at the double bond in the presence of Triton B, while cinnamaldehyde reacts with benzyl mercaptan to form the dibenzyl mercaptal, even in the presence of this catalyst.

In the present work we synthesized the diethyl mercaptals of the following unsaturated aldehydes: cinnamaldehyde (I), 5-phenyl-2,4-pentadienal (II), citral (III), β -cyclocitral (IV), benzaldehyde (V), and furfural (VI). The diethyl mercaptals of benzaldehyde [9] and furfural [7] have been described previously, but their boiling points differed substantially from our data, while no other constants were given in the papers.

The mercaptals of the aldehydes we studied were obtained under mild conditions in high yields and were readily purified by vacuum distillation. The reactions of aldehydes with ethyl mercaptan were carried out in the presence of zinc chloride and in all cases proceeded exclusively at the carbonyl group. The advantage of the synthesis of mercaptals in comparison with acetals is shown particularly clearly by the case of β -cyclocitral. While the diethyl acetal of β -cyclocitral [10] was obtained in low yield and was difficult to separate from the starting aldehyde, its diethyl mercaptal was formed in high yield and was readily purified. The results of the work are given in the table. The condensations of some of the mercaptals we synthesized with α, β -unsaturated ethers will be described in subsequent communications.

EXPERIMENTAL

Synthesis of diethyl mercaptals. To a mixture of 0.27 mole of ethyl mercaptan, 2.5 g of anhydrous zinc chloride, and 2.5 g of anhydrous sodium sulfate, cooled to -2° , was added 0.1 mole of the aldehyde dropwise at such a rate that the temperature did not rise above zero. After the addition of the aldehyde, the mixture was kept in a refrigerator for 20 hr and poured into iced water and the liberated oil extracted with ether. The ether solution was washed twice with a 10% solution of alkali and then water and dried over sodium sulfate. After removal of the ether, the residue was vacuum distilled. The yields and constants of the compounds obtained are given in the table.

Synthesis of Diethyl Mercaptals $\text{RCH}(\text{SC}_2\text{H}_5)_2$

R	Yield %	B.p., °C (P, mm Hg)	M.p., °C	n_D^{20}	d_4^{20}	^{13}C		H		S	
						Found	Calcu- lated	Found	Calcu- lated	Found	Calcu- lated
I 	73,5	134—135 (0, 5)	—	1,5938	1,0512	76,94	73,55	7,63 7,39	7,61	26,42 26,88	26,90
II 	55,1	183—187 (2, 5)	49—50,5	—	—	—	—	7,78 7,83	7,63	24,21 24,39	24,23
III 	70,1	98—100 (0,08)	—	1,5248	0,9589	82,58	81, 3	10,13 10,40	10,14	24,50 24,47	24,81
IV 	68,1	106—107 (0,18)	—	1,5359	1,0031	80,34	79,57	10,02 10,12	10,14	23,86 23,70	24,81
V 	77,5	129—129 (3)	—	1,5725	1,0570	66,14	64,78	7,66 7,75	7,60	30,56 30,44	30,20
VI 	74,9	80— 82 (0,07)	—	1,5458	1,0967	58,40	57,65	6,92 6,90	6,97	31,34 31,35	31,70

* The reaction mixture was kept at 0° for 45 hr.

SUMMARY

The diethyl mercaptals of cinnamaldehyde, 5-phenyl-2,4-pentadienal, citral, and β -cyclocitral were synthesized and characterized.

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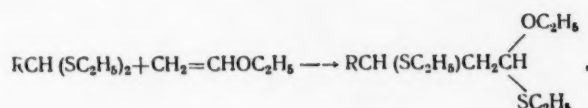
CONDENSATION OF MERCAPTALS WITH VINYL ETHYL ETHER

B. M. Mikhailov and G. S. Ter-Sarkisyan

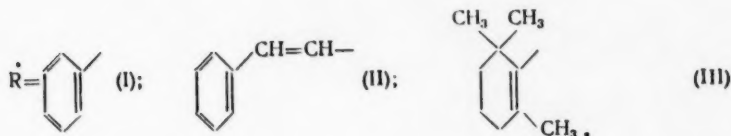
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 10, pp. 1888-1891, October, 1960
Original article submitted March 23, 1960

The condensations of mercaptals with vinyl ethyl ether have not been studied previously. An attempt to condense the diethyl mercaptal of acetaldehyde with vinyl ethyl ether led to a low-molecular polymer of vinyl ethyl ether with a terminal mercaptal group [1].

In the present work we studied the condensations of the diethyl mercaptals of benzaldehyde, cinnamaldehyde, and β -cyclocitral, which we synthesized previously [2], with vinyl ethyl ether. The reactions were carried out in the presence of boron trifluoride etherate or zinc chloride and gave monothioacetals of mercaptoaldehydes according to the scheme:






where



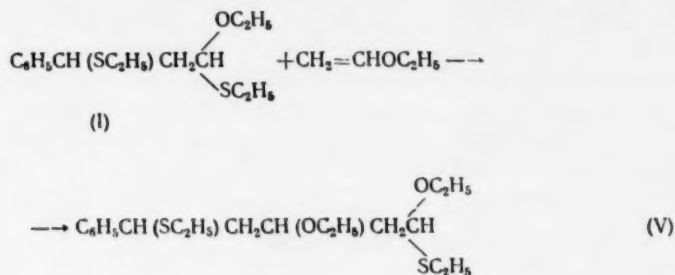
The diethyl mercaptals of benzaldehyde and cinnamaldehyde reacted with vinyl ethyl ether with more difficulty than the diethyl acetals of these aldehydes [3, 4]. With a rise in the reaction temperature, there was an increase in the formation of products from the addition to the mercaptal of two, three, and more molecules of vinyl ethyl ether.

The mixed acetals of mercaptoaldehydes were stable, readily distillable compounds with an unpleasant odor. The presence of the mercaptal group and ethylmercapto groups at a carbon atom attached by a double bond determined the reactions with mercuric chloride in alcohol. This reaction has been proposed for the quantitative determination of alkylmercapto groups in vinyl thioethers [5] and mercaptals [5, 6]. Like ethoxyacetals, monothioacetals of mercaptoaldehydes were converted to unsaturated aldehydes by boiling with glacial acetic acid. Thus, from 1-ethoxy-1,3-di(ethylmercapto)-3-phenylpropane (I) we obtained cinnamaldehyde and from 1-ethoxy-1,3-di-(ethylmercapto)-5-phenyl-4-pentene (II) we obtained 5-phenyl-2,4-pentadienal. By hydrolysis of (I) in the presence of 2,4-dinitrophenylhydrazine, without preliminary elimination of ethyl mercaptan, it was possible to isolate the 2,4-dinitrophenylhydrazone of 3-phenyl-3-ethylmercaptoanal (IV), which was converted to cinnamaldehyde 2,4-dinitrophenylhydrazone by boiling with an alcohol solution of HCl. These reactions demonstrate the structure of the compounds obtained. It seemed interesting to determine how a second molecule of vinyl ethyl ether added to monothioacetals. For this purpose we used the reaction of (I) with vinyl

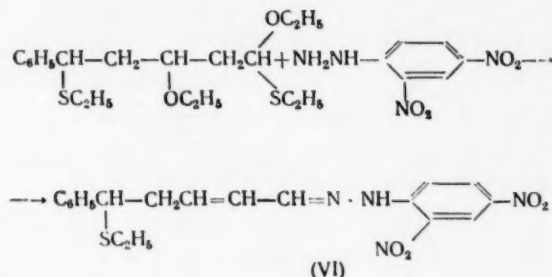
$$\begin{array}{c} \text{SC}_2\text{H}_5 \\ \diagup \\ \text{CH}-\text{CH} \\ \diagdown \\ \text{SC}_2\text{H}_5 \end{array}$$
 Synthesis of Monothioacetals R

R	Reaction conditions		Yield, %	B.p., °C (p. mm Hg)	n_D^{20}	d_4^{20}	MR		C		H		S		C, H, S	
	catalyst	Temp., °C					Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
	$\text{BF}_3(\text{OC}_2\text{H}_5)_2$	0-2	42.4	113-115 (0.08)	1.5370	1.0305	86.23	84.89	63.17 63.33	63.38	8.46 8.55	8.50	21.97 22.20	22.50	21.22 21.19	42.94
	ZnCl_2	28-30	24.1	158-160 (0.12)	1.5591	1.0400	96.56	94.2	65.60 65.77	65.74	8.21 8.25	8.44	—	—	38.92 38.78	39.36
	ZnCl_2	22-24	35.5	126-127 (0.09)	1.5200	0.9954	101.00	99.58	65.50 65.66	65.39	10.20 10.36	10.36	19.50 19.76	19.40	39.51 39.76	40.40

ethyl ether. It was found that the ethylmercapto rather than the ethoxyl group was eliminated to form a new monothioacetal, namely, 1,3-diethoxy-1,5-di(ethylmercapto)-5-phenylpentane (V).



The structure of (V) was demonstrated by the fact that it contained one labile mercapto group (reaction with mercuric chloride) and by the preparation from it of the 2,4-dinitrophenylhydrazone of 5-phenyl-5-ethylmercapto-2-pentalen (VI), which was then converted to the 2,4-dinitrophenylhydrazone of 5-phenyl-2,4-pentadienal.



EXPERIMENTAL

Condensation of diethyl mercaptals with vinyl ethyl ether. To a mixture of 0.2 mole of the diethyl mercaptal and the catalyst (0.5 g of BF_3 etherate or 7 ml of 10% solution of zinc chloride in ethyl acetate) was added 0.1 mole of vinyl ethyl ether dropwise at such a rate that the temperature did not rise above the given value.

After the addition, the mixture was stirred for a further 40 min at the same temperature and then mixed with ether. The ether solution was washed with 5% alkali solution and then water, and dried over sodium sulfate, the ether removed, and the residue fractionated in vacuum. The reaction conditions, yields (on the mercaptal reacting), and constants of the compounds obtained are given in Table 1.

Cinnamaldehyde. A mixture of 12 g of (I), 20 ml of glacial acetic acid, and 2 g of sodium acetate was boiled in a stream of nitrogen for 6 hr, cooled, and poured onto ice and the liberated oil extracted with ether. We obtained 2.9 g (52.1%) of cinnamaldehyde with b. p. 163-165° (35 mm); the 2,4-dinitrophenylhydrazone had m. p. 251-253°. Literature data [7]: m. p. 252-253°.

5-Phenyl-2,4-pentadienal. A mixture of 5 g of (II), 8 ml of acetic acid, and 0.8 g of sodium acetate was boiled in a stream of nitrogen for 3 hr. The normal treatment yielded 0.8 g (32%) of 5-phenyl-2,4-pentadienal with b. p. 110-115° (0.4 mm); the 2,4-dinitrophenylhydrazone had m. p. 199-200°. Literature data [3]: m. p. 200-202°.

2,4-Dinitrophenylhydrazone of 3-phenyl-3-ethylmercaptopropanal IV. To 1.1 g of (I) was added 10 ml of a 20% alcohol solution of mercuric chloride, the precipitate of ethylmercaptomercuric chloride removed by filtration, and an alcohol solution of 2,4-dinitrophenylhydrazine added to the filtrate. Several recrystallizations of the hydrazone from a mixture of alcohol and ethyl acetate and then from alcohol yielded the 2,4-dinitrophenylhydrazone of 3-phenyl-3-ethylmercaptopropanal (IV) as orange crystals with m. p. 100-103°. Found: C 53.86; H 4.68; S 8.46%. $\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_4\text{S}$. Calculated: C 53.56; H 4.85; S 8.56%.

When a solution of 0.2 g of (IV) in 5 ml of alcohol was boiled with 0.5 ml of hydrochloric acid for 1.5 hr, we obtained 0.14 g of cinnamaldehyde 2,4-dinitrophenylhydrazone with m. p. 249-250°.

Condensation of 1-ethoxy-1,3-di(ethylmercapto)-3-phenylpropane with vinyl ethyl ether. Over a period of 30 min, 2.8 g (0.039 mole) of vinyl ethyl ether was added to a mixture of 22.2 g (0.078 mole) of (I) and 0.3 g of BF_3 etherate at 20-22°. The mixture was stirred for a further 30 min at the same temperature and treated as described above. Two vacuum distillations of the residue yielded: 1) 16.6 g of the starting material with b. p. 108-113° (0.09 mm); n_D^{20} 1.5330; 2) 1.2 g (17.1% yield, calculated on the mercaptal reacting) of 1,3-diethoxy-1,5-di(ethylmercapto)-5-phenylpentane (V) with b. p. 158-160° (0.1 mm); n_D^{20} 1.5260; d_4^{20} 1.0254; Found MR 106.74; Calculated MR 105.01. Found: C 63.88; H 9.21; S 17.58; $\text{C}_{15}\text{H}_{18}\text{S}_2$ 16.86%. $\text{C}_{15}\text{H}_{18}\text{O}_2\text{S}_2$. Calculated: 64.00; H 9.02; S 18.00; $\text{C}_2\text{H}_5\text{S}$ 34.35%.

2,4-Dinitrophenylhydrazone of 3-ethoxy-5-ethylmercapto-5-phenyl-2-pentenal (VI). Under the conditions described above, from 1.2 g of (V) we obtained 0.8 g of a mixture of the 2,4-dinitrophenylhydrazones of 5-phenyl-5-ethylmercapto-2-pentenal (VI) and 5-phenyl-2,4-pentadienal, and several recrystallization of this from a mixture of ethyl acetate and alcohol and then from alcohol yielded (VI) as lustrous orange crystals with m. p. 149-151.5°. Found: S 7.63; 7.76; N 14.03; 14.19%. $\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}_4\text{S}$. Calculated: S 8.08; N 13.99%. After boiling a solution of 0.2 g of (VI) in 15 ml of alcohol with a few drops of HBr for 3 hr, we obtained 0.12 g of the 2,4-dinitrophenylhydrazone of 5-phenyl-2,4-pentadienal with m. p. 200-202° [3].

SUMMARY

1. The condensation of the dimethyl mercaptals of cinnamaldehyde, benzaldehyde, and β -cyclocitral with vinyl ethyl ether in the presence of acid catalysts was studied.
2. As a result of these reactions with one molecule of vinyl ethyl ether we obtained monothioacetals of mercaptoaldehydes $\text{RCH}(\text{SC}_2\text{H}_5)\text{CH}_2\text{CH}(\text{OC}_2\text{H}_5)\text{SC}_2\text{H}_5$.
3. The addition of a second molecule of vinyl ethyl ether to 1-ethoxy-1,3-di(ethylmercapto)-3-phenylpropane resulted in elimination of the alkylmercapto group and formed 1,3-diethoxy-1,5-di(ethylmercapto)-5-phenylpentane.

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SOME PROBLEMS IN THE MECHANISM OF METHYLCYCLOHEXANE CONVERSIONS OVER NICKEL-ALUMINA CATALYST AT A HIGH HYDROGEN PRESSURE

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 10, pp. 1891-1894, October, 1960

Original article submitted March 25, 1960

In previous work [1] we studied the hydrodemethylation of methylcyclohexane in the presence of nickel catalysts. It was shown that over a nickel-alumina catalyst there is a series of other conversions in addition to demethylation of methylcyclohexane. A detailed study of the hydrodemethylation of methylcyclohexane and the conversions of the hydrocarbons thus formed is not only of substantial importance for directing demethylation, but also of theoretical interest.

In the present work we investigated the conversions of cyclohexane, methylcyclopentane, and toluene over a nickel-alumina catalyst. A detailed study was made of the composition of the catalyzates obtained and also that of the catalyzate obtained previously [1] in the study of the conversions of methylcyclohexane.

EXPERIMENTAL

The starting hydrocarbons had the properties presented in Table 1. The experiments were carried out in a flow apparatus [2] at 360° and a hydrogen pressure of 20 atm in the presence of 10% Ni-Al₂O₃ catalyst. The starting hydrocarbons were passed at a space velocity of 0.2 hr⁻¹ with a molar ratio of hydrogen to hydrocarbon of 4 : 1.

TABLE 1

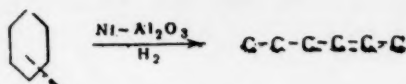
Hydrocarbons	B. p., °C (760 mm)	n_D^{20}	d_4^{20}
Cyclohexane	80,6	1,4261	0,7784
Methylcyclo- pentane	71,8	1,4096	0,7484
Toluene	110,6	1,4966	0,8673

The catalyzates obtained in experiments with cyclohexane and methylcyclopentane were analyzed by gas-liquid chromatography [3]; the catalyzates obtained in experiments with methylcyclohexane and toluene were analyzed by a combined method of chromatographic adsorption on silica gel, sharp fractionation, gas-liquid chromatography, and dehydrogenation of the six-membered rings over a Pt-C-Fe catalyst [4]. The results of investigating the composition of the catalyzates are given in Table 2.

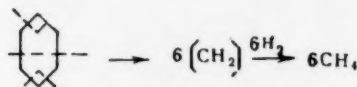
The data obtained show that cyclohexane is dehydrogenated to benzene and also isomerized to methylcyclopentane under the conditions used. The ratio of the yields of the three hexanes obtained as a result of opening of the methylcyclopentane ring on the Ni-Al₂O₃ catalyst under a hydrogen pressure agree with the observations of previous authors on the hydrogenolysis of a pentamethylene ring in the presence of Pt-C [5] and a skeletal nickel catalyst [6], when a methyl group attached to the pentamethylene ring has a shielding effect on hydrogenolysis of the C-C bonds of the ring.

It is noteworthy that n-hexane was formed from cyclohexane in a greater amount than from methylcyclopentane. This indicates that in the presence of the Ni-Al₂O₃ catalyst, the cyclohexane molecule apparently

partially undergoes direct ring opening with the formation of n-hexane.

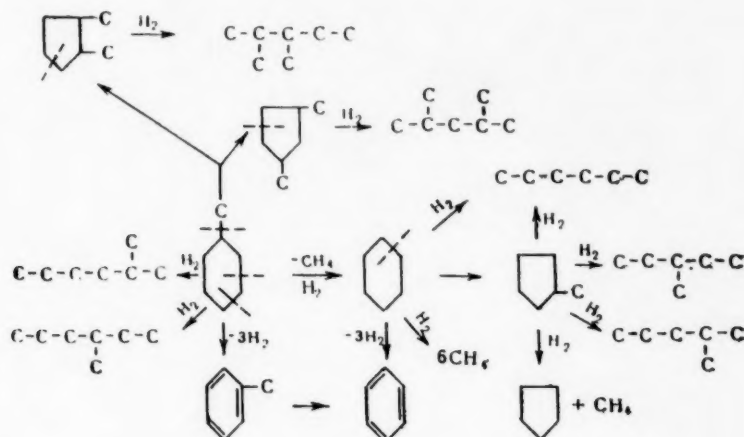


However, this hypothesis does not exclude the mechanism proposed by one of us [7], which consists of simultaneous rupture of all bonds of the six-membered ring with the formation of methane, as the emergent gases consisted largely of hydrogen and methane.



It must be assumed that these two processes may occur in parallel under the conditions used. In the catalyze from methylcyclohexane we detected an appreciable amount of 3-methylhexane and 2-methylhexane. It is possible that, in the hydrogenolysis of methylcyclohexane and methylcyclopentane on a $\text{Ni}-\text{Al}_2\text{O}_3$ catalyst, the methyl group has a shielding effect on the direction of opening of the C-C bonds of the ring. The data in Table 2 also show that, in the case of toluene, the total yield of demethylation products, i. e., benzene and cyclohexane, is less than from methylcyclohexane under the same conditions. It is probable that the $\text{C}_{\text{arom}}-\text{C}_{\text{aliph}}$ bond is broken with greater difficulty than the $\text{C}_{\text{aliph}}-\text{C}_{\text{alicycl}}$ bond under the conditions used.

On the basis of the investigation, we propose the following scheme of conversions of methylcyclohexane on a Ni-Al₂O₃ catalyst at a high hydrogen pressure.



SUMMARY

1. An investigation was made of the conversions of cyclohexane, methylcyclopentane, and toluene in the presence of a Ni-Al₂O₃ catalyst at 360° (20 atm), a molar ratio of hydrogen to hydrocarbon of 4 : 1, and a space velocity of 0.2 hr⁻¹.
2. Under these conditions of catalytic hydrogenolysis of the side group, there were certain side reactions of methylcyclohexane involving contraction of the six-membered to a five-membered ring and partial hydrogenolysis of both the five-membered and six-membered rings.

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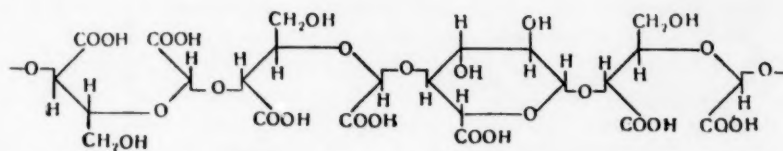
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OXIDATION OF DICARBOXYCELLULOSE BY NITROGEN OXIDES

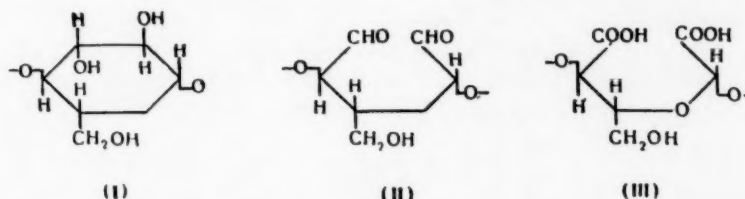
N. Ya. Lenshina, V. S. Ivanova, and V. I. Ivanov

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 10, pp. 1894-1896, October, 1960
Original article submitted March 29, 1960

By the action of nitrogen oxides on dialdehydocellulose preparations, we previously [1] prepared cellulose derivatives, which are called tricarboxycelluloses and, from the chemical point of view, consist of a polyacetal of glyoxylic, erythronic, and glucuronic acids (scheme 1).



By the action of nitrogen oxides on dialdehydocellulose with the theoretical content of aldehyde groups (36.9 % CHO), we prepared for the first time [2] practically pure polyacetal of glyoxylic and erythronic acids. Data on the oxidative conversions of dialdehydocellulose under the action of nitrogen oxides led us to the conclusion that a typical oxidation at C₆ [3] in an opened pyran ring (scheme 2, II)* is extremely difficult. On the basis of experimental data, we established that the oxidation of primary hydroxyls in dialdehydocellulose preparations by nitrogen oxides under static conditions occurs in glucose residues with a pyran ring. The hypothesis was put forward that opening of the pyran ring affects oxidation of hydroxyls at C₆. To confirm this hypothesis, we then carried out experiments on the oxidation by nitrogen oxides of dicarboxycellulose preparations, which contain an opened pyran ring with carboxyl groups at C₂ and C₃ (scheme 2, III). Our hypothesis on the effect of the pyran ring is confirmed by the analogous behavior of low-molecular compounds.



Thus, in the oxidation of linear alcohols [4] by nitrogen oxides there is no specific oxidation of the primary hydroxyl (traces of acids) in comparison with cyclic compounds, for example, methyl glucoside. However, it should be emphasized that in the oxidation of polyuronic acids [5, 6], oxidation at C₂ and C₃ is essentially unhindered.

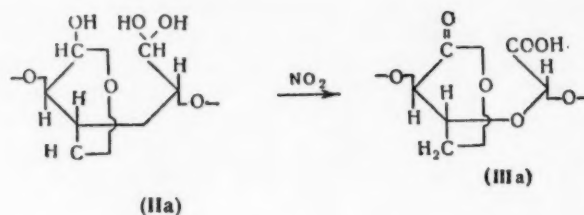
* The acetal oxygen is omitted from formulas I, II, and IIa.

Table of Oxidation of Dicarboxycellulose Samples No. 1 and 2 by Nitrogen Oxides under Static Conditions

Oxidation time, hr.	Carboxyl group content after oxidation by nitrogen oxides, %			I/S
	total	uronic (I)	nonuronic (S)	
Dicarboxycellulose 1 (10% of COOH groups)				
3	12,8	3,5	9,3	0,38
24	21,8	13,0	8,8	1,47
48	25,1	14,5	10,6	1,40
Dicarboxycellulose 2 (22% of COOH groups)				
12	24,5	2,1	22,4	0,09
24	26,6	3,1	23,5	0,13
72	26,1	3,9	22,2	0,17

EXPERIMENTAL

Purified cotton cellulose was oxidized successively under normal conditions with sodium periodate and chlorite [7] to yield dicarboxycellulose preparations with different carboxyl group contents. The samples obtained were then oxidized with nitrogen oxides (1 part of NO_2 per part of sample by weight) under static conditions at room temperature for various times. The data are given in the table. As the data in the table show, the content of nonuronic carboxyl groups at C_2 and C_3 was practically the same before and after oxidation with nitrogen oxides. This indicates that there was practically no oxidation by nitrogen oxides at C_6 in fragments with an open pyran ring (scheme 2, III). As is shown by the ratio I/S (see table), the increase in total carboxyls is mainly because of uronic carboxyls, i. e., because of oxidation of hydroxyls at C_6 in fragments with a pyran ring (scheme 2, I). The inhibition of oxidation of the hydroxyl at carbon atom 6 in an open pyran ring may be explained both by opening of the ring and by the state of the functional groups or both these factors. The data on the oxidation of dialdehyde- and dicarboxycelluloses by nitrogen oxides show that oxidation at C_6 is very strongly hindered regardless of the chemical nature of the functional groups at C_2 and C_3 of the opened pyran ring.



The formation of C_3 - C_6 hemiacetals (scheme 3, IIa) [8] and lactones (schemes 2 and 3, IIIa) [9] under the conditions of oxidation by nitrogen oxides (acid medium) converts the hydroxyl group at C_6 in dialdehyde- and dicarboxycellulose preparations, respectively, from the free to the bound state.

SUMMARY

In the oxidation of dicarboxycellulose by nitrogen oxides there is very strong hindrance to typical oxidation at C_6 in the anhydroglucose units in fragments with an open pyran ring.

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SIMPLE SYNTHESIS OF TRIALLYLBORON AND SOME OF ITS CONVERSIONS

L. I. Zakharkin and V. I. Stanko

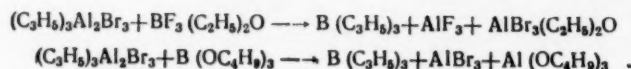
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

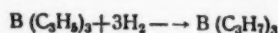
No. 10, pp. 1896-1898, October, 1960

Original article submitted March 30, 1960

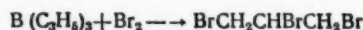
Triallylboron was obtained for the first time quite recently from triallyl borate and allylmagnesium bromide in 33% yield [1]. Topchiev et al. [2-4] recently obtained triallylboron in up to 92% yield by adding a mixture of allyl bromide and boron trifluoride etherate to magnesium. Mikhailov and Tutorskaya [5] reported that the yield of triallylboron from allylmagnesium bromide and boron trifluoride etherate is 68%. In the present work, we found that triallylboron is obtained more conveniently from allylaluminum sesquibromide, which is formed smoothly from allyl bromide and aluminum in the presence of diethyl ether [6]. Triallylboron is formed by the reaction of allylaluminum sesquibromide with an alkyl borate or boron trifluoride etherate according to the following scheme:



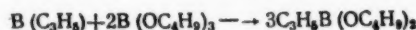
The use of allylaluminum sesquibromide does not require large amounts of absolute ether and guarantees reproducible yields of triallylboron of 78-80% of theoretical. In the work of Topchiev et al. [3] and Mikhailov and Tutorskaya [5] it was shown that the C-B bond in triallylboron has a high lability. We also studied some conversions of triallylboron. When hydrogenated over a skeletal catalyst at room temperature under pressure, triallylboron added three moles of hydrogen and was converted to tripropylboron.



It was found in contrast to the data of Topchiev et al. [3], triallylboron reacts readily with bromine even at -35°, when there is rupture of the C-B bond and the addition of bromine to the double bonds to form 1,2,3-tribromopropane as the main product.



When triallylboron was heated with tributyl borate, disproportionation occurred with the formation of dibutyl allylborate.



Triallylboron reacts with mercurous chloride in aqueous solution apparently with the formation of allylmercuric chloride, which, however, could not be isolated in a pure form. In the reaction of triallylboron with thallium trichloride in aqueous solution, the latter was converted quantitatively to thallium monochloride.

EXPERIMENTAL

Preparation of triallylboron. To 15 g of aluminum turnings, 0.1 g of mercuric chloride, and 75 ml of absolute ether stirred in a nitrogen atmosphere was gradually added 91 g of allyl bromide at 35-40°. After the allyl bromide had been added, the mixture was stirred at 45-50° for three hr until the aluminum had dissolved almost completely. The solution obtained was added dropwise with stirring to 28.4 g of boron trifluoride etherate at such a rate that the temperature remained at 55-60°. After the reaction mixture had been heated at this temperature for a further 3 hr, the ether was removed and the triallylboron distilled from the residue over the range 45-74° (20-25 mm). Redistillation yielded 21 g (78% of theoretical) of triallylboron with b. p. 59-61° (21 mm).

To allylaluminum sesquibromide (from 15 g of aluminum turnings and 91 g of allyl bromide) in 75 ml of absolute ether was added 46 g of butyl borate dropwise with stirring at 50-55°. The mixture was heated at 55-60° for 6 hr. Redistillation of the crude products in vacuum yielded 22.5 g (80.5% of theoretical) of triallylboron. The triallylboron was distilled on a column with a glass packing (25 theoretical plates): b. p. 52.5-53° (18 mm); 153.5-154° (720 mm); n_D^{20} 1.4512; d_4^{20} 0.7745. Literature data [3]: b. p. 155°; 44-46° (10 mm); n_D^{20} 1.4500; d_4^{20} 0.7689 [2]; b. p. 62-65° (15 mm); d_4^{20} 0.7178.

Hydrogenation of triallylboron. Into a 150-ml autoclave, which had been flushed with nitrogen, were placed 13.4 g (0.1 mole) of triallylboron in 70 ml of hexane and 5 g of skeletal nickel catalyst in the form of lumps 5 x 5 mm in size. The hydrogen pressure was adjusted to 30 atm. After 3 hr, ~7 liters of hydrogen had been absorbed. After removal of the hexane, the tripropylboron distilled at 156-157°; n_D^{20} 1.4128. We obtained 9.0 g. Literature data [7]: b. p. 156°; n_D^{20} 1.41352.

Reaction of triallylboron with butyl borate. A mixture of 6.7 g (0.05 mole) of triallylboron and 23.0 g (0.1 mole) of butyl borate was heated for 16 hr at 160-170° in a nitrogen atmosphere. The mixture was distilled on a fractionating column with a glass packing (25 theoretical plates) in vacuum. We isolated 24 g of dibutyl allylborate with b. p. 104-104.5° (19 mm); n_D^{20} 1.4228; d_4^{20} 0.8404. Literature data [5]: b. p. 98-100° (15 mm); n_D^{20} 1.4230; d_4^{20} 0.8413.

Reaction of triallylboron with bromine. With stirring and cooling to -30 to -35°, 48.0 g (0.3 mole) of bromine in 20 ml of chloroform was added dropwise to 6.7 g (0.05 mole) of triallylboron in chloroform. After being stirred for 3 hr, the reaction mixture was left overnight. The chloroform and unreacted bromine were removed by distillation and the residue was vacuum distilled. We obtained as the sole product 21 g (51% of theoretical) of 1,2,3-tribromopropane with b. p. 65-67° (2 mm); m. p. 16.5°. The residue was a tar.

An analogous experiment was carried out with a triallylboron to bromine ratio of 1 : 3. The whole of the bromine reacted. Distillation of the reaction products yielded only 1,2,3 - tribromopropane and a large tarry residue. Literature data [8]: m. p. 16-17°.

Reaction of triallylboron with mercuric chloride. To a solution of 5.5 g of mercuric chloride in 40 ml of water was added 2.1 g (0.1 mole) of triallylboron with stirring in a nitrogen atmosphere. A precipitate formed immediately. This was collected and washed with hot water. The solid did not crystallize from chloroform and ethanol, began to melt at 70°, and remained turbid even at 100°. Found: C 10.60; H 1.51; Hg 72.17; Cl 14.89%, C_3H_5HgCl . Calculated: C 12.99; H 1.81; Hg 72.34; Cl 12.81%. The structure of the substance was not established.

Reaction of triallylboron with thallium trichloride. To a solution of 2.2 g (0.007 mole) of thallium trichloride in 50 ml of water was added 1.34 g of triallylboron. Thallium monochloride precipitated quantitatively from the reaction medium and was collected and washed with hot pyridine. After drying in vacuum, the thallium chloride had m. p. 429-430°. Literature data [9]: m. p. 430°.

SUMMARY

1. A simple method was developed for the preparation of triallylboron from allylaluminum sesquibromide and butyl borate or boron trifluoride etherate.
2. Some reactions of triallylboron were studied.

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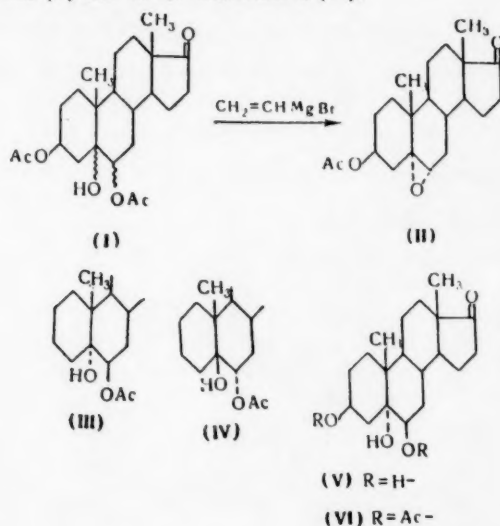
NEW CASE OF CLOSURE OF A 5α , 6α -OXIDE RING IN
THE ANDROSTANE SERIES

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 10, pp. 1898-1899, October, 1960
Original article submitted July 5, 1960

Two of us [1] recently described a new method of forming an α -oxide ring by the reaction of the 3,6-diacetate of androstane- 3β ,5,6-(trans)-triol-17-one (I) with vinylmagnesium bromide. The starting material (I) was obtained by the method of Ehrenstein, who assigned it the configuration of a 3β , 5β , 6α -triol [2, 3]. However, the observed reaction excludes this configuration, which would be unreactive under the given conditions as follows from the material below. The most probable mechanism for this reaction is the conversion of the free hydroxyl at C-5 to an alcoholate anion under the action of the Grignard reagent in the first stage. The alcoholate anion then displaces the 6-acetoxy group by a bimolecular reaction to form the α -oxide ring. The basic condition for this ring closure is that the two substituents should be in a diaxial position and this is only fulfilled in the case of the 5α -hydroxy- 6β -acetoxy derivative (III). The 5β -hydroxy- 6α -acetoxy derivative (IV), in which the two substituents occupy an equatorial position, does not satisfy this condition. For this reaction to occur, it is necessary that the hydroxyl group at C-5 and the acetoxy group at C-6 occupy an anti-parallel position and all four reaction centers (5-one, C-5, C-6, 6-OAc) lie in one plane [4]. The cessation of reaction at the oxide stage under mild conditions, which was observed previously [1], may be explained by the fact that the approach of the Grignard reagent to the side opposite to the oxygen [5] is hindered by the angular methyl group at C-10.

The above unequivocally demonstrates that Ehrenstein's "trans-triol" [2, 3] has the configuration of androstane- 3β , 5α , 6β -triol-17-one (V) and its 3,6-diacetate is (VI).



It is therefore necessary to reexamine the configurations of the *trans*-triol adopted in previous publications [1-3]. In one of his later publications [6], Ehrenstein assigned the right configuration to the substance (I) without correcting his previous data. There are later reports [7-9] on the possibility of opening of the 5,6-oxide ring to a *trans*-glycol with a 6 β -hydroxyl group. It is interesting to note that closure of the oxide ring was not observed under the action of potassium bicarbonate solution on (I); instead, in this case there was normal hydrolysis of the acetoxy group with the formation of the known androstane-3 β ,5 α ,6 β -triol-17-one (VII) with m. p. 290°. The 3,6-diacetate of androstane-3 β ,5 α ,6 α -triol-17-one (VIII) (*cis*-triol) reacts normally with vinylmagnesium bromide to give the monoacetate of 17-vinylandrostane-3 β ,5 α ,6 α ,17 β -tetraol (IX) [10].

EXPERIMENTAL

3 β -Acetate of 5 α ,6 α -oxidoandrostane-3 β -ol-17-one (II). To a solution of vinylmagnesium bromide in tetrahydrofuran (THF) from 0.3 g of magnesium and 4 ml of vinyl bromide in 9.5 ml of THF at -15° to -20° were added 10 ml of anhydrous ether and 500 mg of the 3,6-*trans*-diacetate (I) (m. p. 212-214°) in 8 ml of THF and 20 ml of anhydrous ether. The mixture was stirred for 6 hr at -15° and left overnight. On the following day the reaction mixture was stirred and boiled gently (37°) for 2 hr, cooled, treated with 2 g of ammonium chloride and 10 g of ice, and extracted with ether and the extract dried with magnesium sulfate. After removal of the solvents, the residue (530 mg) was recrystallized from ether. We isolated 300 mg of the substance (II) with m. p. 218°, which did not depress the melting point of an authentic sample. A mixture with the starting diacetate (I) melted at 180°. By chromatography on Al₂O₃ (elution with a benzene-ether mixture), from the mother solution we isolated an additional 70 mg of (II) with m. p. 220°. The yield was 90% of theoretical. Found: C 72.81; 73.03; H 8.55; 8.73%; C₂₁H₃₀O₄. Calculated: C 72.80; H 8.73%. When the vinylmagnesium bromide was replaced by ethylmagnesium bromide in ether at room temperature, the yield of (II) fell to 40%.

Androstane-3 β ,5 α ,6 β -triol-17-one (VII). A mixture of 140 mg of the 3,6-diacetate (I), 20 ml of methanol, 200 mg of potassium bicarbonate, and 4 ml of water was boiled under reflux for 45 min. The alcohol was then removed in vacuum and the crystalline residue collected, washed with water on the filter, and dried. We obtained 100 mg of androstane-3 β ,5 α ,6 β -triol-17-one in the form of colorless crystals with m. p. 290° (from alcohol). A mixture with the 5,6-oxide (II) melted at 212-230°.

Monoacetate of 17-vinylandrostane-3 β ,5 α ,6 α ,17 β -tetraol (IX). The reaction of vinylmagnesium bromide (0.4 g of magnesium) and the 3,6-diacetate of the *cis*-triol (VIII) (450 mg) was carried out as described above. The normal treatment (see previous experiment) yielded an oily product (480 mg), which was chromatographed on Al₂O₃ (elution with benzene-ether). We isolated 190 mg of a crystallization oil. Three recrystallizations from an acetone-hexane mixture yielded the monoacetate of 17-vinylandrostane-3 β ,5 α ,6 α ,17 β -tetraol (IX) with m. p. 168-169°. Found: C 70.12; 70.48; H 9.26; 9.43%; C₂₃H₃₆O₅. Calculated: C 70.37; H 9.24%.

SUMMARY

1. A new case of closure of an α -oxide ring in the reaction of the 3,6-diacetate of androstane-3 β ,5 α ,6 β -triol-17-one with vinylmagnesium bromide and ethylmagnesium bromide is described.
2. The configuration of the 3,6-diacetate of androstane-3 β ,5,6-(*trans*)-triol-17-one is corrected.
3. The mechanism and stereochemistry of closure of the 5 α ,6 α -oxide ring are discussed.

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LETTERS TO THE EDITOR

NEW METHOD OF SYNTHESIZING UNSATURATED ACIDS

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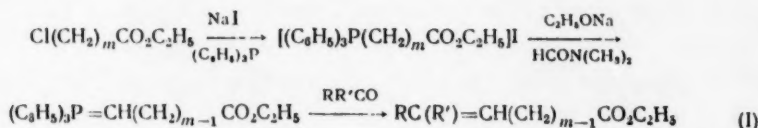
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 10, p. 1900, October, 1960

Original article submitted May 26, 1960

Unsaturated acids of the general formula $RC(R') = CH(CH_2)_{2n+1}COOH$ ($n \geq 3$) are widely distributed in nature and play an important part in the metabolism of plants and animals [1]. The synthesis of these acids presents considerable difficulties [2] and up to now it has been impossible to synthesize many of them.

We developed a new method of preparing acids of this type, based on the Wittig reaction:



($m \geq 3$). By this method we were able to prepare ylides from phosphonium salts of esters of higher ω -halo acids, which do not undergo the Wittig reaction under normal conditions. Thus, from pelargonaldehyde and ethyl ω -chlorodecanoate we obtained a 67% yield of ethyl eicosen-11-oate [(I), $R = n-C_8H_{17}$, $R' = H$, $m = 10$, b. p. 171-173° (1 mm); n_D^{20} 1.4530; d_4^{20} 0.8736], whose cis-isomer has been isolated from the oil of the seeds of different plants of the mustard family. From ethyl ω -chlorononanoate and enanthol we synthesized the ethyl ester of hexadecen-9-oic acid [(I), $R = n-C_6H_{13}$, $R' = H$, $m = 8$, b. p. 134-135° (1 mm); n_D^{20} 1.4488; d_4^{20} 0.8746; yield 51%], whose cis-isomer (palmitoleic acid) is present in almost all known fats and phosphatides [1]. Analogously, from ethyl ω -chloroundecanoate and butyl methyl ketone, we obtained ethyl 12-methylhexadecen-11-oate [(I), $R = n-C_4H_9$, $R' = CH_3$, $m = 10$, b. p. 143-145° (1 mm), n_D^{20} 1.4670; d_4^{20} 0.8920; yield 47%].

Since ω -chloro-substituted acids are readily accessible at the present time [3], the method proposed offers wide possibilities for the preparation of various ethylene and polyene acids and also acids with a branched chain.

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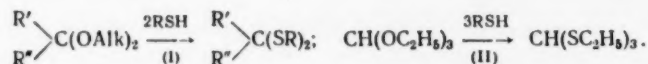
METHOD OF PREPARING MERCAPTOLS AND TRITHIOALKYL
ESTERS OF ORTHOFORMIC ACID

M. F. Shostakovskii, A. V. Bogdanova, G. I. Plotnikova,
and A. N. Dolgikh

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 10, p. 1901, October, 1960
Original article submitted June 11, 1960

In studying the reaction of mercaptans with alkoxy derivatives of vinyl and ethylvinyl ethers and thioethers [1], we found that the alkoxy groups in acetals, ketals, and also ethyl orthoformate are readily replaced by the mercaptoalkyl radicals of mercaptan. We obtained good yields of various mercaptals [2], mercaptols, and trithioalkyl esters of orthoformic acid. In most cases, the methods of preparing these compounds given in the literature are complex and give low yields of the final products [3, 4].

Mercaptals of various ketones and trithioalkyl esters of orthoformic acid were obtained readily and in good yield by the method we propose:



Heating 5 g of the diethyl ketal of acetone and 5 g of ethyl mercaptan in a sealed ampoule at 120-130° for 12 hr with subsequent distillation yielded 5.05 g (80.7% of theoretical) of the diethyl mercaptol of acetone (I). B. p. 77.5-78° (15 mm); n_D^{20} 1.4950, d_4^{20} 0.9460. Found: C 51.21; 51.17; H 9.72; 9.84; S 38.80; 38.73%. $\text{C}_7\text{H}_{16}\text{S}_2$. Calculated: C 51.17; H 9.82; S 39.03%.

From a mixture of 4.7 g of triethyl orthoformate and 11.2 g of ethyl mercaptan under the same conditions we obtained 1.2 g of the starting ester and 4.0 g (87% of theoretical) of the trithioethyl ester of orthoformic acid (II). B. p. 144° (26 mm); n_D^{20} 1.5405; d_4^{20} 1.0555. Found: C 42.79; 42.86; H 8.34; 8.37; S 45.78; 48.51%. $\text{C}_7\text{H}_{16}\text{S}_3$. Calculated: C 42.81; H 8.21; S 48.97%. A 0.1737-g sample required 26.48 ml of 0.1 N NaOH, which corresponds to 99.81% of thioester.

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HYDROLYSIS OF p-NITROPHENYL ACETATE IN THE
PRESENCE OF N-CARBOBENZOXY-ASPARAGYLSERYLGLYCINE

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 10, pp. 1901-1902, October, 1960

Original article submitted July 12, 1960

Peptides forming part of the active centers have been isolated from the hydrolysis products of a series of proteases and esterases acylated with labeled organophosphorus compounds. In a number of cases, these peptides contained fragments with the same sequence of amino acids, namely, glycylasparagylserylglycyl. The unusual properties of the serine hydroxyl in the active center probably make it responsible for the formation of the enzyme-substrate complex.

In order to check the catalytic activity of low-molecular peptides present in active centers of enzymes, we synthesized the ethyl ester of N-carbobenzoxy-D,L-(β -methyl)-asparagyl-D,L-seryglycine (Z-ASG). We studied the effect of Z-ASG on the rate of hydrolysis of p-nitrophenyl acetate in the system phosphate buffer (0.06 M) pH 7.0-alcohol (1 : 1) at 37.5°. It was found that the rate of hydrolysis of p-nitrophenyl acetate in the presence of Z-ASG fell in proportion to the concentration of Z-ASG (with the inhibition rate constant $k_{\text{inhib}} = 3.4 \cdot 10^{-2} \text{ sec}^{-1} \cdot \text{mole}^{-1}$). In the presence of imidazole, which catalyzes basic hydrolysis of p-nitrophenyl acetate, the inhibiting action of Z-ASG was found to be even more appreciable ($k_{\text{inhib}} = 4.2 \cdot 10^{-2}$ and $1.75 \cdot 10^{-1} \text{ sec}^{-1} \cdot \text{mole}^{-1}$) at imidazole concentrations of $5 \cdot 10^{-5}$ and $5 \cdot 10^{-4}$ M. Z-ASG also retards the alcoholysis of p-nitrophenyl acetate in the presence of imidazole. The addition of N-carbobenzoxy-D,L-seryl-glycine did not affect the rate of hydrolysis of p-nitrophenyl acetate. The authors consider that the inhibition of p-nitrophenyl acetate hydrolysis is connected with the high affinity of the serine hydroxyl in Z-ASG for the carbonyl group of carboxylic acid derivatives.

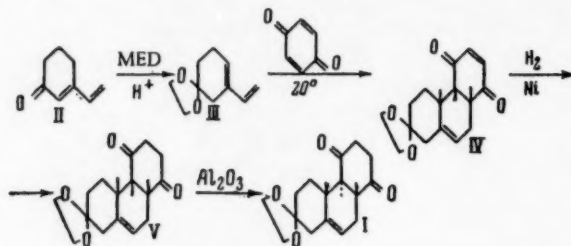
SYNTHESIS OF THE 2-ETHYLENE KETAL OF ANTI-TRANS-
 Δ^{10} -DODECAHYDROPHENANTHRENE-2,5,8-TRIONE

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 Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
 No. 10, p. 1902, October, 1960
 Original article submitted July 18, 1960

During work on the synthesis of steroids and related compounds, we prepared the diketone (I), which is possibly intermediate for the synthesis of 19-norsteroids with an oxygen function at C₁₁.

Exchange ketolization of 3-vinyl- Δ^2 -cyclohexenol (II) [1] with methylethyldioxolane (MED) [2] proceeded with migration of the α, β -double bond [3] and led to the diene ketal (III) (53% yield; b. p. 69-71° (0.5 mm), n_D^{22} 1.5162. The latter condensed smoothly with quinone to give the adduct (IV) (87% yield; m. p. 165-166°), whose structure was demonstrated by conversion to 2-hydroxyphenanthrene.



Hydrogenation of the adduct (IV) gave the diketone (V) (80% yield; m. p. 155.5-157°) with the original syn-cis configuration and, by contact with alkaline alumina, this was isomerized to the diketone (I) (88% yield; m. p. 154.5-155°), which depressed the melting point of the diketone (V) and had the "natural" anti-trans configuration.

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A GERMANIUM ANALOG OF CARBENES

M. E. Vol'pin and D. N. Kursanov

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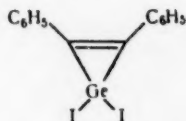
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 10, p. 1903, October, 1960

Original article submitted July 19, 1960

Together with Koreshkov, we showed previously that the action of the dihalocarbenes CCl_2 and CBr_2 on tolan forms derivatives of the three-membered aromatic cyclopropenylium system [1].

In view of the similarity in the electronic structure of derivatives of divalent germanium and divalent carbon (carbenes), we studied the reactions of divalent germanium compounds with substances containing multiple carbon-carbon bonds. By heating GeI_2 with tolan, we obtained a stable addition product with m. p. 300.5-303° (corr.) with the composition $\text{C}_{14}\text{H}_{10}\text{GeI}_2$ (Calculated: C 33.32; H 2.00; I 50.29; Ge 14.39%; Found: C 33.18; 33.15; H 1.93; 2.04; I 50.43; 50.29; Ge 14.47; 14.59%) and the probable structure (I).



The substance obtained was soluble in benzene, carbon tetrachloride, and alcohol and insoluble in heptane, ether, and water. The action of silver nitrate on an alcohol solution of the substance slowly produced a precipitate of silver iodide. Both the iodine atoms were replaced by ethyl groups by the action of ethylmagnesium bromide and by oxygen by the action of alkali.

Thus, it may be assumed that the addition of GeI_2 to the triple bond of tolan proceeds analogously to the addition of dihalocarbenes with the formation of a germanium analog of the aromatic cyclopropenylium system.

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REACTIONS OF 1,3-DIOXOLANES WITH α, β -UNSATURATED ETHERS

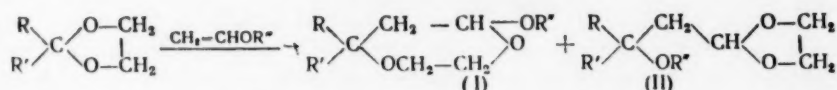
B. M. Mikhailov and L. S. Povarov

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 10, pp. 1903-1904, October, 1960

We found that some derivatives of 1,3-dioxolane are capable of reacting with α, β -unsaturated ethers in the presence of catalysts of the BF_3 type to form a mixture of isomeric addition products of types (I) and (II).



The structure of the addition products was established by the liberation of the corresponding carbonyl derivatives during hydrolysis.

From 2-phenyl-1,3-dioxolane and vinyl ethyl ether we obtained a fraction with b. p. 83-88° (1.5 mm); yield 36%. Found: C 70.25; 70.45; H 8.51; 8.44%. $\text{C}_{13}\text{H}_{18}\text{O}_3$. Calculated: C 70.24; H 8.16%. The hydrolysis of this fraction yielded 3-(β -hydroxyethoxy)-3-phenylpropanal with m. p. 71°, corresponding to the structure of the addition product of type (I), and 3-ethoxy-3-phenylpropanal, whose 2,4-dinitrophenylhydrazone had m. p. 112°, corresponding to the product with the structure (II). From 2-methyl-1,3-dioxolane and vinyl ethyl ether we obtained a product with b. p. 112-116° (72 mm); yield 56.8%. Found: C 60.30; 60.41; H 10.05; 10.24%. $\text{C}_8\text{H}_{16}\text{O}_3$. Calculated: C 59.97; H 10.07%. From the same dioxolane and vinyl butyl ether we obtained a product with b. p. 95-97° (9 mm); yield 50.5%. Found: C 63.78; 63.80; H 10.60; 10.73%. $\text{C}_{10}\text{H}_{20}\text{O}_3$. Calculated: C 63.79; H 10.71%. The reaction of 2,2-dimethyl-1,3-dioxolane with vinyl ethyl ether yielded a product with b. p. 118-123° (75 mm); yield 25%. Found: C 62.16; 62.10; H 10.01; 10.01%. $\text{C}_9\text{H}_{18}\text{O}_3$. Calculated: C 62.04; H 10.41%. Condensation of 2-(2,6-dimethylheptadien-1,5-yl)-1,3-dioxolane, obtained from citral and ethylene glycol, with vinyl ether yielded a product with b. p. 114-118° (1.5 mm); yield 18%. Found: C 71.42; 71.44; H 10.62; 10.72%. $\text{C}_{16}\text{H}_{28}\text{O}_3$. Calculated: C 71.60; H 10.52%. In the case of unsubstituted 1,3-dioxolane, 2-methyl-2-phenyl-1,3-dioxolane, and the ethylene ketal of β -ionone, it was impossible to isolate addition products in appreciable amounts.

CURRENT EVENTS

ELECTION OF ACADEMICIANS AND CORRESPONDING MEMBERS OF THE ACADEMY OF SCIENCES USSR

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1905-1908, October, 1960

The regular election of academicians and corresponding members was held in the Academy of Sciences USSR. Eleven candidates were nominated and registered for the three vacancies (one academician and two corresponding members) announced on April 9, 1960 in the Division of Chemical Sciences; there were three candidates for the position of academician and six for corresponding members of the Academy of Sciences USSR in the field of "The Chemistry of High-Molecular Compounds" and two candidates for corresponding members in the field of "The Chemistry of Natural and Biologically Active Compounds." Four candidates were nominated and registered for the corresponding member vacancy in the field of chemistry in the Siberian Division of the Academy of Sciences USSR. The general meeting of the Academy of Sciences on June 10 of this year confirmed the choice of the Division of Chemical Sciences of M. M. Koton and N. K. Kochetkov as corresponding members and the choice of the Siberian Division of the Academy of Sciences USSR of B. V. Ptitsyn and M. F. Shostakovskii as corresponding members, as recommended by the Division of Chemical Sciences.

CORRESPONDING MEMBER OF THE ACADEMY OF SCIENCES, USSR IN THE FIELD "THE CHEMISTRY OF HIGH-MOLECULAR COMPOUNDS"



KOTON, Mikhail Mikhailovich—a well-known scientists in the field of organic chemistry and the chemistry of high-molecular compounds. Beginning in 1938, he has been carrying out extensive investigations of the effect of the structure of monomers on the polymerization capacity and on the properties of the polymers obtained for solving the important problem of synthesizing polymers with given properties. M. M. Koton and his co-workers were the first to make a detailed study of substituted amides of acrylic and methacrylic acids and on this basis, new methods were developed for the synthesis of highly heat-resistant polymers with rings in the chain; he also prepared new styrenes with two, three, and four substituents in the nucleus, which are of interest as heat-resistant, high-frequency dielectrics. In recent year, metal-containing styrenes and methacrylates with a high thermal stability and other important properties have been prepared for the first time under the direction of M. M. Koton. These investigations enabled M. M. Koton to develop theoretical ideas on the effect of chemical structure on the polymerization capacity, heat-resistance, and dielectric properties of substituted

styrenes. M. M. Koton produced new dielectrics for capacitor production and also developed and applied an original method of preparing highly efficient scintillating plastics based on polystyrene for recording radioactive radiations. At the present time, M. M. Koton and his co-workers together with branch institutes are introducing into industry a new polymeric material of the "pentone" type, which has high strength and heat and chemical resistance.

M. M. Koton has made a large group of investigations on the chemistry of organometallic compounds; he studied the reactivity of various organic derivatives of mercury, lead, tin, bismuth, arsenic, antimony, and silicon. Together with G. A. Razuvaev, he put forward and checked with a large amount of experimental material the hypothesis of the free radical mechanism of reactions of organometal compounds in solution. M. M. Koton discovered a new reaction for the mercuration of organic compounds (phenols, anilines, etc.). The investigations of K. A. Andrianov and M. M. Koton on the preparation of high-molecular substances consisting of polysiloxane chains connected by organic radicals initiated the applied chemistry of organosilicon compounds. M. M. Koton has published more than 130 scientific works, including the textbook "Chemistry of Organic Dielectrics" (1957).

CORRESPONDING MEMBER OF THE ACADEMY OF SCIENCES, USSR
IN THE FIELD "THE CHEMISTRY OF NATURAL AND BIOLOGICALLY
ACTIVE COMPOUNDS"

KOCHETKOV, Nikolai Konstantinovich—an outstanding organic chemist whose main field is the chemistry of natural compounds. Most of the scientific work of N. K. Kochetkov has been devoted to biogenic polymers, the search for natural and synthetic substances with a high physiological activity, and the study of the relation between biological action and chemical structure. The result of this work over many years has been new methods



of synthesis and the technological development of a series of valuable medicinal preparations; the antitubercular drug, thianide, the effective preparation for the treatment of epilepsy, chloracon, and the antihistaminic with a prolonged action, diazoline; he discovered a new drug against parkinsonism, phenacon, powerful ganglion-blocking agents of a fundamentally new type, namely, amines with a branched chain and he first achieved the synthesis of an important antitubercular antibiotic, cycloserine. The production of all these preparations either has been developed or is being developed at the present time. N. K. Kochetkov has combined the practical trend of these investigations with a detailed study of the chemistry of the corresponding classes of compounds, in particular, the chemistry of cycloserine. As a result of an extensive study of the relation of antimicrobial action to chemical structure, he predicted and then demonstrated experimentally that cycloserine is a powerful inhibitor of transamination enzymes. A similar thorough study has been made of other compounds, namely γ -carbolines, a large number of aliphatic-aromatic amines, etc. At the present time N. K. Kochetkov is concentrating his attention on a new field, namely, the chemistry of carbohydrates and nucleotides. He is carrying out investigations on the chemistry of the polymers of very great

biological importance, desoxyribonucleic acids and glycopeptides, and the chemistry of specific polysaccharides of blood plasma and is studying natural stimulants of the central nervous system present in ginseng and *Schizandra chinensis*.

The scientific interests of N. K. Kochetkov extend far beyond the limits of the chemistry of natural and biologically active substances and cover the development of various sections of organic chemistry. His work

on the chemistry of β -chlorovinyl ketones is of the greatest importance and here he devised about 20 new methods of synthesizing various types of aliphatic, alicyclic, aromatic, and heterocyclic compounds. N. K. Kochetkov discovered and made a detailed study of a new type of tautomerism and also studied the mechanism of the exchange of a halogen at an unsaturated carbon atom etc. He has published more than 160 scientific works and wrote a textbook on the chemistry of natural compounds (together with I. V. Torgov and M. M. Botvinik).

SIBERIAN DIVISION OF THE ACADEMY OF SCIENCES USSR

CORRESPONDING MEMBERS OF THE ACADEMY OF SCIENCES, USSR IN THE FIELD "CHEMISTRY"

PTITSYN, Boris Vladimirovich—a highly qualified inorganic chemist with a wide range of interests. His main scientific work has been devoted to the chemistry of complex compounds, analytic chemistry, and radiochemistry. He has studied the properties of complex compounds of divalent platinum, methods of determining the instability constants of complex compounds, and the properties of some complex compounds of uranium. A series of studies on the oxidation-reduction properties of complex compounds of platinum metals enabled him to develop volumetric methods for determining platinum and iridium in various valence states in the presence of other platinum metals. These methods are used in the platinum industry.



At the present time B. V. Ptitsyn is carrying out work on oxidation-reduction systems that are of theoretical and practical interest in analytical chemistry, problems in the theory of 2nd order electrodes, namely, determination of the limits of applicability of these electrodes, and the analytical chemistry of halogens. He is also concerned with the problem of protecting man from the action of radioactive isotopes by searching for methods for discharging them from the human organism. As a result of investigations it was found that radioactive strontium, yttrium, and zirconium are practically completely absorbed in a short time by synthetic hydroxyapatite from aqueous solutions and gastric juice. Thus, this preparation may be recommended as a prophylactic in possible contamination by radioactive strontium, yttrium, and zirconium.

B. V. Ptitsyn has published more than 60 scientific works.

* * *

SHOSTAKOVSKII, Mikhail Fedorovich—a well-known organic chemist. M. F. Shostakovskii was a student of A. E. Favorskii and has continued his work on the chemistry of acetylene, creating a new field in organic chemistry, namely, the chemistry of vinyl ethers; he has developed methods for the synthesis of various vinyl compounds and devised a theory of vinylation (Favorskii-Shostakovskii reaction). The vinylation method he developed forms the basis of a new technology, involving the use of acetylene under pressure. M. F. Shostakovskii has made extensive investigations of the properties of vinyl compounds, their reactivity, and the relation of the latter to the structure of the substances. His investigations of polymerization and copolymerization of vinyl compounds have extended ideas on the theory of polymerization processes and also made it possible to prepare practically important polymeric products. The large amount of experimental data he has obtained has led to

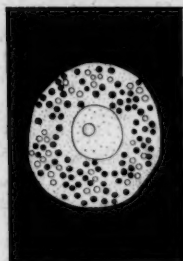
the conclusion that vinyl compounds containing O, S, and N have a dual reactivity and react both by ionic and by free-radical mechanisms. M. F. Shostakovskii developed the oxonium theory of the conversion of vinyl ethers. According to this theory, the initial reaction of vinyl ethers with a catalyst forms unstable oxonium complexes, which on decomposing, initiate various reactions. In recent years, M. F. Shostakovskii has been in-



vestigating new organosilicon compounds. The application of vinylation in this field has made it possible to prepare vinyl compounds of silicon from acetylene and silanes. At the present time he is developing a new trend, namely, the chemistry of diacetylene and methylacetylene.

M. F. Shostakovskii's investigations are characterized by a close link with various fields of industry and technology. The highly effective therapeutic preparation "Shostakovskii's balsam" has found wide application in the war years and at the present time. "Vinipol", an additive for improving the properties of oils, which he prepared, is produced on an industrial scale. Valuable lacquers and adhesives were prepared from copolymers of vinyl ethers and some unsaturated compounds. The technology of the production of a valuable product, namely polyvinylpyrrolidone, which is used in medicine as a blood substitute and also for removing toxic substances from the organism, was developed under his direction.

M. F. Shostakovskii has published more than 200 scientific works, including three monographs. About 30 inventions belong to him.



ACHIEVEMENTS IN SOVIET MICROBIOLOGY

Edited by A. A. Imshenetskii

Director of the Institute of Microbiology
of the Academy of Sciences of the USSR

TRANSLATED FROM RUSSIAN

(Original published for the Institute
of Microbiology,
Academy of Sciences of the USSR,
by the Academy of Sciences Press,
Moscow)

This concise survey of recent developments in (as well as projected directions of) Soviet microbiology is divided into four major sections:

I. Progress in General Microbiology, *A. A. Imshenetskii*
A broad review which enables the Western scientist to see clearly the direction in which Soviet microbiologists are making their studies.

II. Achievements of Soviet Microbiology in the Field of the Study of the Geological Activity of Microorganisms, *S. I. Kuznetsov*

In a field which has not been widely considered by Western scientists, this paper indicates great advances made in the USSR. The use of microorganisms in petroleum research and recovery are discussed, as are Soviet efforts to classify precisely and map out geologic or ecologic microbiological strata as they occur in the geologist's scheme. This article summarizes Soviet research into the relationships of various groups of microorganisms to geological — petroleum — inorganic substrates environments.

III. Forty Years of Technical Microbiology in the USSR, *V. N. Shaposhnikov, N. D. Ierusalimskii, and I. L. Rabotnova*

Noteworthy in this paper (which deals with fermentation microbiology, acetone-butanol, organic acids, riboflavin, antibiotics, etc.) is Shaposhnikov's description of disagreement in the USSR, as there has been in the West, on the biosynthesis of citric acid by various species of *Aspergillus*.

IV. Achievements in the Field of Soil Microbiology in the USSR, *E. N. Mishustin*

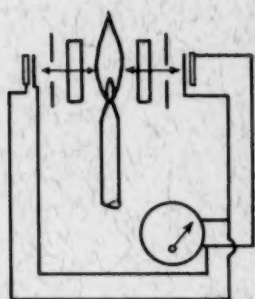
Soviet research in this area places particular emphasis on rhizosphere, root nodule, and nitrogen-fixing bacteria, and on the relationship between higher plants and associated microorganisms. Special attention is given to Vinogradskii's early description of auxotrophs and Krasilnikov's recent classification of actinomycetous microorganisms. Some comment is made on methodology, especially microbial counts and selection techniques.

82 pages

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TECHNIQUES IN FLAME PHOTOMETRIC ANALYSIS

by N. S. Poluéktov

TRANSLATED FROM RUSSIAN

Original published by the
State Scientific-Technical Press
for Chemical Literature, Moscow

This volume contains a practical and comprehensive survey of the techniques employed and the instruments required for this important rapid analysis method, as well as a brief account of the theoretical principles involved. Experimental procedures and the design of apparatus are discussed at length, making the relevant chapters a valuable manual for all chemists concerned with analytical problems.

The second half of the book deals with the determination of individual elements in a variety of materials, providing much factual information, together with a complete and international bibliography. There are many useful tables, and two appendices which consider wavelengths of brightest spectral lines and peaks of molecular bands of elements excited in flame, and recommended wavelengths of spectral lines and peaks of molecular bands for determination of elements with the aid of a spectrophotometer employing glass optics and using an air-acetylene flame.

Scientists working in the varied fields in which flame photometry is today applicable — in geochemistry and mineralogy for the analysis of waters and minerals, in agrochemistry for the determination of metabolic bases in soils and the analysis of fertilizers and plant materials, in biochemistry and medicine for the investigation of urine, blood serum, and tissues, in industry for production control by analysis of metal alloys, glasses, cements, refractories, reagents, etc. — will find

TECHNIQUES IN FLAME PHOTOMETRIC ANALYSIS
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